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THE ABSORPTION OF LIGHT BY WATER CHANGED BY THE PRESENCE OF STRONGLY HYDRATED SALTS, AS SHOWN BY THE RADIOMICROMETER— NEW EVIDENCE FOR THE SOLVATE THEORY OF SOLUTION

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The use of the radiomicrometer in studying the absorption spectra of certain substances has already been discussed by Jones and Guy.[1] The radiomicrometer was used in the study of absorption spectra of solutions, rather than the grating spectrograph and the photographic plate, because the radiomicrometer enabled us to measure not only the positions of the different lines and bands, but also to study quantitatively their intensity. Further, the radiomicrometer, as has already been pointed out, enables us to study the absorption spectra of solutions over a much greater range of wave lengths than the photographic method.

In building a radiomicrometer that would be adapted to this work, that is, with sufficient sensibility and with a short period, one of the greatest difficulties encountered was to ob-

[1] Physik. Z., **13**, 649 (1912).

tain copper wire free from iron. This was a necessity, since the presence of an appreciable quantity of iron in the copper gave rise to a "magnetic control" which rendered the instrument unstable and the zero point inconstant. This difficulty was for the most part overcome, due to the kindness of Messrs. Leeds and Northrup, of Philadelphia, and of R. W. Paul, of London. They both furnished us with copper wire so free from iron that the "magnetic control" could easily be regulated. By means of this wire and the thermoelectric junction already described,[1] a most sensitive radiomicrometer which at the same time had a very short period was built. Work with salts of neodymium and praseodymium, the results of which were recorded in the *Physikalische Zeitschrift*, was done with this instrument.

At the beginning of the present academic year the absorption spectra of solutions of a large number of salts of different metals were mapped out. The spectra of these salts were compared with the absorption of water, using the same depths of water as the water in the various solutions. It was soon found that the absorption of the solution was *less*, and in some cases *very much less*, than that of the layer of water having a depth equal to the depth of the water in the solution. The depth of water in the solution was determined from the concentration of the solution and from its specific gravity.

It is obvious that the above is a very remarkable fact. The dissolved substance could not have less than no absorption of light, the assumption having been made, up to this time, that in an aqueous solution the water present absorbs just as much as pure uncombined water. The above result is directly at variance with everything that was known at the time.

It became at once obvious that we could not measure the absorption spectrum of a solution, subtract from it the absorption due to water, and conclude that the remainder was the absorption due to the dissolved substance, since the water in the solution has very different absorption from an equal amount of pure, uncombined water.

[1] Physik. Z., **13**, 651 (1912).

We then carried out a number of experiments in cells whose depths could be easily and accurately adjusted, with different substances, in the following manner: We measured the absorption spectra of a number of different substances. We then measured the absorption spectra of water having the same depths of layer as the water in the solutions. We found that for certain substances the pure water was more opaque than the solutions, and for other substances the water was more transparent. The percentage transmission, that is, the deflection of the radiomicrometer for the solution, divided by the deflection for water, for the first named substances amounted to more than one hundred per cent. Pure water had a different absorption from an equal depth of water in the solution, and since this difference varied from one dissolved substance to another, it is obvious that this method was not the one to be followed. It would be very difficult, not to say impossible, to interpret the results obtained by dividing the radiomicrometer deflection for the solution by those for pure water. We should simply be obtaining the transmission of the solution in terms of pure water, which was not what was desired.

What we want to know is the actual absorption or transmission of the solution, and then that of pure water having a depth of layer that was just equal to that of the water in the solution. These two sets of results could then be compared with one another.

In this earlier work we had, however, noted that solutions of those substances which are largely hydrated are more transparent than pure water having the depths of the water in the solutions in question. Solutions of nonhydrated substances, or of only slightly hydrated substances, provided the substances themselves do not absorb light, are not more transparent than pure water having the same depths as the water in the solution.

It would seem from this observation that water combined with the dissolved substance had less absorption of light than pure, uncombined water. To test this quantitatively the following procedure was adopted:

A solution of the substance in question was prepared of known concentration and its specific gravity determined. This solution was placed in one cell, set to a depth of say 2 mm. Some of the same solution was then placed in another cell set to a depth of say 1 mm. Light of given, known wave length was then passed through the one solution and the deflection noted. Light of this same wave length was then passed through the other solution, and the deflection in this case also noted. The deflection produced when the deeper solution was in the path of the beam of light was then divided by the deflection produced when the shallower solution was in the path of the light, and this gave the absolute transmission of the solution of the substance in question of known concentration, having a depth of layer of 20 mm. This process was repeated for the different parts of the spectrum, changing the wave length of light from reading to reading by only a small amount. Light of any given wave length was always passed through the one solution, and then, at once, through the other solution of a different depth. The object in using the two depths of the same solution, and then dividing the deflection produced by the deeper layer by that obtained when the more shallow layer was in the path of the beam of light, was to eliminate any effect of reflection from the glass ends closing the cells containing the solutions, and also to eliminate any changes in the total amounts of energy sent through the solution, due to slight changes in the intensity of the Nernst glower.

From the specific gravity of the solution and its known concentration, the amount of water in a layer of the solution, say 21 cm. in depth, could easily be calculated. Similarly, the amount of water in a layer of the solution which was 1 mm. deep could also be calculated. Water was then introduced into the two cells, and these cells so adjusted that the difference in the depth of the two was exactly equal to the depth of the water in the layer of the solution which was 20 mm. deep.

The deflection for the water in the deeper cell was then read for any given wave length of light, and then, at once,

the deflection when the light was passed through the *more shallow* layer of water. The deflection for the deeper layer was divided by the deflection for the more shallow layer. This operation was repeated for the various wave lengths of light in the manner just described. The result was the absolute transmission for water with a depth of layer just equal to the depth of water in the solution in question.

The above results for the solution are plotted as one curve, and those for water having the same depth as the water in the solution as another curve, wave lengths being abscissas and transmission ordinates. A comparison of the two curves shows at once whether water in the free, uncombined condition or the same depth of water in the solution in question is the more transparent.

The data obtained by dividing the deflections produced by the deeper solutions by those for the more shallow, and, similarly, by those for water, are also given in the following tables. These are the data from which the accompanying curves were plotted.

The substances studied were chosen from the standpoint of their power to solvate or to combine with the solvent in which they were dissolved. In all of the work recorded in this paper the solvent used was water. We were practically limited, in this phase of the work, to those substances which themselves have little or no power to absorb light. We were limited to those substances that are both colorless in the visible part of the spectrum, and have little or no absorption in the regions in which the absorption bands of water occur.

We selected for these substances with little or no hydrating power salts of potassium and ammonium. The potassium salts studied were the chloride and nitrate. Ammonium chloride and nitrate were also investigated. We selected for the salts with large hydrating power calcium chloride, magnesium chloride and aluminium sulphate. These salts were shown by the earlier work in this laboratory, which was done shortly after Jones proposed the solvate theory of solutions, using the freezing-point method, to be among the most strongly hydrated substances with which we are familiar.

It will be seen from the following data that two depths of layers of each solution of every substance investigated were employed. The object of this was to bring out the two most important water bands in the region of the spectrum investigated. This could not be done by studying only one depth of solution, since the depth which was necessary and sufficient to bring out clearly one of these water bands would not bring the other out in the way desired. By using the two depths of solution and studying each of them in the manner described above, that is, by the differential method, we were able to investigate both of the water bands as produced, on the one hand, by the pure solvent, and, on the other, by the solution.

In the following tables, under λ are given the wave lengths of light that were passed through the solution, and under I/I_0 the percentage of transmission, on the one hand, of the solution, and, on the other, of water having a depth exactly equal to that of the water in the solution.

The ordinates of the curve, as has already been stated, are percentage transmissions and the abscissas wave lengths.

Table I

	KCl 4N		NH_4Cl 4 N		NH_4NO_3 3.12 N	
λ	I/I_0	H_2O	I/I_0	H_2O	I/I_0	H_2O
710	97	97	92	98	95	98
724	96	95	91	96	97	98
741	95	95	90	92	96	96
760	93	95	85	92	91	95
776	92	95	85	88	92	94
798	94	95	88	95	91	95
818	92	95	87	95	92	96
836	94	93	87	95	91	94
855	91	90	86	93	89	92
878	92	90	86	91	90	93
900	90	89	84	87	89	88
922	87	86	82	86	85	90
947	82	84	79	82	82	83
958	77	78	73	72	73	79
964	75	73	69	70	70	71
969	65	65	64	63	65	67
974	58	56	57	58	58	59

Table I (continued)

979	51	50	52	52	50	54
982	47	46	45	46	44	46
985	41	45	43	43	40	44
991	39	43	41	43	39	43
1007	39	43	41	42	39	44
1013	40	42	39	44	41	44
1019	42	46	40	46	42	44
1025	41	42	44	49	45	48
1032	49	49	44	49	48	49
1037	53	52	56	55	52	53
1042	56	56	53	58	55	55
1046	59	60	57	57	57	60
1059	63	62	58	65	60	65
1065	68	67	62	67	64	65
1072	71	68	64	68	66	69
1078	74	72	67	67	66	72
1085	75	73	67	66	68	74
1100	77	75	68	72	69	78
1113	76	76	69	72	69	78
1138	75	72	68	70	68	72
1148	70	69	64	65	64	71
1158	64	63	62	64	59	64
1165	58	59	58	58	56	60
1172	52	51	50	50	53	52
1179	42	40	40	40	38	41
1186	29	28	29	26	29	30
1193	18	19	19	19	18	19
1200	13	16	14	13	12	17
1206	10	12	12	12	9	13
1213	10	11	10	12	9	13
1220	10	11	10	11	9	12
1227	10	11	10	11	9	12

In the above table the depth of layer of all the solutions was the difference between 21 and 1, i. e., 20 mm. The depth of water was in every case the same as that of the water in the solution in question.

The depth of layer of the following solutions was the difference between 11 mm. and 1 mm., i. e., 10 mm. The depth of water used was in every case the same as that of the water in the solution:

Table II

λ	KCl 4 N I/I_0	H_2O	NH_4Cl 4 N I/I_0	H_2O	NH_4NO_3 3.12 N I/I_0	H_2O
1085	85	86	79	87	81	88
1100	87	88	80	92	81	93
1113	86	87	79	86	84	86
1138	81	85	79	84	81	84
1148	79	82	77	84	78	84
1158	80	79	74	81	76	81
1165	76	77	71	77	72	77
1172	72	71	66	70	67	70
1179	64	62	59	62	61	62
1186	51	51	52	50	50	50
1193	41	43	42	44	40	44
1200	35	38	37	40	34	40
1206	37	36	35	37	32	37
1213	30	34	30	36	32	36
1220	30	35	29	35	34	35
1227	30	34	30	35	32	35
1233	30	33	28	35	31	35
1241	30	34	29	34	31	34
1248	31	34	28	33	31	33
1250	33	34	30	34	32	34
1255	34	35	30	36	32	36
1268	34	35	31	37	32	37
1270	37	31	32	38	33	38
1285	38	38	33	38	33	38
1295	39	38	32	38	33	38
1300	41	38	32	39	34	39
1308	42	39	32	41	35	41
1316	41	39	32	40	34	40
1323	42	37	32	38	34	38
1330	40	37	32	37	33	37
1338	40	35	30	35	31	35
1346	36	33	28	36	30	36
1352	34	29	26	29	27	29
1358	29	26	23	27	25	27
1365	25	22	21	23	21	23
1372	20	18	17	20	17	20
1387	13	12	12	11	10	11
1404	7	7	7	8	7	8
1418	3	4	4	3	3	3
1430	2	2	3	2	2	2
1445	0	0	0	1	1	1

In Table II the depth of layer of the solution that was used was only half of that in Table I. The object of this was to bring out more prominently the second water band.

The depth of layer of the following solutions was the difference between 21 mm. and 1 mm., i. e., 20 mm. The depth of water used in every case was the same as that of the water in the solution:

Table III

	$CaCl_2$ 5.38 N		$MgCl_2$ 4.96 N		$Al_2(SO_4)_3$ 1.02 N	
λ	I/I_o	H_2O	I/I_o	H_2O	I/I_o	H_2O
710	94	98	95	98	95	93
724	92	98	98	98	95	95
741	90	95	95	98	94	93
760	87	94	94	98	92	93
776	88	93	92	97	93	95
798	91	96	93	94	92	90
818	93	99	90	90	93	92
836	92	97	92	95	92	92
855	90	93	91	90	90	91
878	90	90	91	93	91	90
900	89	92	88	92	89	90
922	86	91	88	91	85	86
947	87	84	84	86	82	81
858	78	79	76	78	76	73
964	75	73	82	76	72	66
969	70	68	75	69	68	61
974	65	62	68	65	64	55
979	59	53	61	56	58	48
982	51	49	48	51	53	42
985	48	49	54	45	51	40
991	44	46	48	49	47	39
1007	42	46	46	48	46	38
1013	42	46	45	50	46	39
1019	43	49	44	51	44	40
1025	47	50	46	44	46	43
1032	52	53	51	54	46	45
1037	55	55	52	56	52	50
1042	58	59	56	58	53	53
1046	62	62	59	65	55	55
1059	66	65	63	67	55	58
1065	71	70	69	70	62	63
1072	74	72	71	75	60	65
1078	75	74	71	76	64	69
1085	78	76	76	79	65	70

Table III (continued)

λ	$CaCl_2$ 5.38 N I/I_o	H_2O	$MgCl_2$ 4.96 N I/I_o	H_2O	$Al_2(SO_4)_3$ 1.02 N I/I_o	H_2O
1100	80	77	78	79	67	72
1113	79	78	80	81	67	74
1138	77	75	77	78	64	67
1148	74	71	75	77	60	65
1158	69	65	73	73	57	55
1165	66	62	65	65	55	53
1172	61	52	61	58	50	43
1179	54	41	52	44	45	34
1186	42	30	43	32	34	22
1193	32	21	32	24	25	15
1200	22	17	23	18	20	12
1206	16	16	18	17	16	10
1213	13	15	16	18	14	9
1220	12	13	14	15	11	10
1227	12	13	14	16	12	8

In the following table the depth of layer used was the difference between 11 and 1 mm., i. e., 10 mm. The object of using the smaller depth of the solution was to bring out more clearly in the case of hydrated salts the second water band:

Table IV

λ	$CaCl_2$ 5.38 N I/I_o	H_2O	$MgCl_2$ 4.96 N I/I_o	H_2O	$Al_2(SO_4)_3$ 1.02 N I/I_o	H_2O
1085	84	84	82	84	79	82
1100	84	84	83	84	78	81
1113	84	86	83	84	78	84
1138	86	85	82	83	77	83
1148	82	83	79	80	75	80
1158	80	79	77	77	73	77
1165	78	76	77	75	70	73
1172	76	72	74	70	66	69
1179	72	65	71	64	63	58
1186	63	55	62	52	55	48
1193	54	45	56	46	49	39
1200	45	40	48	42	43	34
1206	38	39	42	40	38	30
1213	35	39	39	38	36	29
1220	33	36	37	38	34	28
1227	32	36	36	38	32	28
1233	31	35	34	37	32	28

Table IV (continued)

1241	32	35	34	34	31	28
1248	32	35	34	37	31	28
1250	33	35	34	38	31	28
1255	33	37	34	38	31	28
1268	35	38	33	38	30	29
1270	37	39	34	39	30	30
1285	38	40	35	40	30	31
1295	40	40	35	40	30	32
1300	42	41	36	41	30	32
1308	42	41	37	42	30	33
1316	45	41	39	42	30	33
1323	47	40	39	41	28	33
1330	46	39	40	40	27	32
1338	45	37	38	38	27	30
1346	42	35	38	36	24	27
1352	40	32	34	33	22	24
1358	37	29	33	30	20	21
1365	33	25	29	26	18	19
1372	29	21	25	22	15	15
1387	19	13	18	15	10	9
1404	12	10	12	11	7	5
1418	7	6	7	9	4	3
1430	3	3	4	3	2	2
1445	2	1	1	1	1	1

When salts which are strongly hydrated in aqueous solution are not very concentrated, the difference between the transparency of the salt solution and that of water of the same depth of layer as the water in the solution is not so pronounced. This is what would be expected, since the total amount of water combined with the dissolved salt increases with the concentration of the solution. The data given in the following table bring out this fact:

Table V

	$CaCl_2$ 2.69 N		$MgCl_2$ 2.48 N		$Al_2(SO_4)_3$ 0.508 N	
λ	I/I_o	H_2O	I/I_o	H_2O	I/I_o	H_2O
710	96	94	95	95	97	96
724	95	96	93	96	98	96
741	95	95	90	95	95	93
760	94	96	92	95	95	95
776	93	97	93	95	95	95
798	90	98	91	95	96	96

Table V (continued)

λ	$CaCl_2$ 2.69 N I/I_o	H_2O	$MgCl_2$ 2.48 N I/I_o	H_2O	$Al_2(SO_4)_3$ 0.508 N I/I_o	H_2O
818	93	97	91	93	95	96
836	91	96	89	93	93	95
855	91	92	88	92	92	92
878	90	92	84	90	90	91
900	88	90	84	88	89	86
922	89	92	81	86	82	85
947	82	86	78	83	78	80
958	75	79	72	76	73	75
964	70	74	70	73	68	69
969	65	69	62	64	62	62
974	58	61	58	58	57	54
979	50	52	50	51	50	46
982	44	47	46	46	46	42
985	40	43	42	43	43	40
991	39	41	40	41	41	39
1007	38	40	41	42	40	40
1013	39	42	40	44	40	40
1019	40	43	40	44	41	41
1025	43	45	44	41	43	43
1032	45	47	47	44	45	46
1037	48	50	50	46	47	48
1042	51	52	52	48	49	49
1046	56	56	56	54	53	54
1059	61	59	58	55	60	59
1065	65	64	64	62	59	62
1072	69	67	67	64	63	65
1078	70	69	69	67	65	69
1085	72	72	72	68	68	72
1100	73	73	73	71	69	73
1113	72	74	74	72	68	74
1138	72	74	74	70	67	72
1148	66	69	69	67	64	67
1158	67	62	62	60	58	62
1165	57	58	58	58	54	54
1172	52	51	53	52	47	46
1179	46	39	42	42	39	35
1186	30	27	31	27	28	25
1193	20	19	21	20	20	16
1200	13	14	15	15	14	12
1206	12	11	12	13	12	10
1203	11	11	12	12	11	10
1220	11	10	11	11	11	10
1227	10	9	10	10	10	9

The depth of layer of the different solutions for which the results are recorded in the above table was the difference between 21 and 1 mm., i. e., 20 mm. The results are, therefore, comparable with those recorded in Table III, the difference being a difference in the concentrations of the solutions used. It will be seen from a glance at the table that the difference between the transmission of the solution and that of water at the same depth as the water in the solution is very much less for the more dilute than for the more concentrated solutions. As has already been pointed out, this is exactly what would be expected in terms of the solvate theory applied to the phenomenon in question.

Considerable work was done in *comparing directly* the transmission of a solution and that of water having the same depth as the water in the solution in question. The deflection of the radiomicrometer as given by the solution is in the column marked "*I* sol." and the deflection as given by water having the same depth as water in the solution is given in the column marked "I_o H_2O."

The results obtained for aluminium sulphate having a concentration 1.02 N and for 4 N potassium chloride are given in the following table. The depth fof solution used was 20 mm. and the depth of water that o the water in the solutions in question.

Table VI

λ	*I* sol. $Al_2(So_4)_3$	I_o H_2O	*I* sol. KCl	I_o H_2O
710	50	51	53	53
724	58	58	56	56
741	62	63	67	68
760	72	72	77	77
776	75	76	88	90
798	83	83	98	99
818	82	82	108	109
836	93	94	116	116
855	97	97	124	124
878	105	105	129	130
900	105	105	140	138
922	112	112	140	140
947	113	113	142	142
958	109	106	136	136

Table VI (continued)

λ	I sol. $Al_2(SO_4)_3$	I_0 H_2O	I sol. KCl	I_0 H_2O
964	107	100	129	125
969	104	93	118	116
974	98	83	108	106
979	93	73	92	92
982	82	66	83	83
985	80	64	78	80
991	78	62	78	80
1007	78	65	78	81
1013	74	65	81	85
1019	77	68	84	88
1025	80	75	96	96
1032	84	77	100	101
1037	91	84	112	108
1042	92	92	119	116
1046	99	99	125	120
1059	105	105	141	136
1065	109	112	150	145
1072	114	119	159	153
1078	118	125	164	158
1085	122	132	168	164
1100	128	140	176	172
1113	129	142	178	175
1138	127	142	174	170
1148	123	131	164	162
1158	112	118	161	159
1165	108	111	157	154
1172	99	94	132	126
1179	87	74	107	100
1186	68	49	73	66
1193	54	35	50	48
1200	42	26	24	36
1206	35	23	39	32
1213	30	21	25	30
1220	28	20	24	29
1227	26	19	24	28
1241	24	19	23	26
1255	23	18	25	27

In this work duplicate measurements were made with the radiomicrometer for nearly every solution of all the substances worked with at the various wave lengths studied. It was found that the readings for the different

solutions of the same substance having the same concentration were, for a given wave length, different from one another to the extent of somewhat less than 2 per cent. From this it seems fair to assume that the error in our work was not greater than 2 per cent.

An examination of the tables of data for potassium chloride, ammonium chloride and ammonium nitrate, that is, for those substances which, in aqueous solutions, combine with very little water, as was demonstrated by the freezing-point method, shows that for all wave lengths studied the solution and water of the same depth as the water in the solution have practically the same transmission. The dissolved substance does not combine with the solvent water, and the water in the solution has almost exactly the same effect upon light as so much pure water would have. This is exactly what would be expected from our knowledge of the absorption of light by dissolved substances and by the solvent. When we began this work we supposed that the water in the solution, whether it was combined with the dissolved substance or not, would have the same power to absorb light as so much pure solvent water. We shall now see that such is not the case.

The results for the above named substances were not plotted in the form of curves, since the curve for water and for the solution would practically coincide with one another, the dissolved substance having very little absorption over the region of wave lengths studied in this investigation.

When we turn to the data in Tables III and IV very different relations manifest themselves. These are the data for calcium chloride, magnesium chloride and aluminium sulphate, that is, for salts which, in aqueous solution, are strongly hydrated, as was shown by the earlier work in this laboratory.[1] The solution in these cases is often more transparent than the same amount of water that is contained in the solution.

That these relations may appear the more clearly, the results obtained for the above named salts are plotted as curves in Figs. I to VI. Fig. I is the curve for calcium chloride

[1] Carnegie Institution of Washington, Publication No. 60.

having a depth of 20 mm. This was obtained by dividing the deflection produced by 21 mm. of the solution by that produced by 1 mm. of the solution. On the same sheet we have the curve for water having a depth equal to that of the water in the calcium chloride. This curve for water was also obtained by the "differential" method, i. e., by dividing the deflections produced by the deeper solution by those obtained with the more shallow solution, the difference in the depths of water in the two cases being just equal to the depth of water in 20 mm. of the solution in question. Fig. II is the curve for calcium chloride with a depth of layer of 10 mm. (11–1). The data from which the curve was plotted are contained in Table IV. The smaller depth of solution was used so that the water band between 1.2μ and 1.3μ would come out more distinctly. The results for this solution, like those for all the others, are compared with the absorption of a depth of water equal to that of the water in the solution. The absorption of the water in this, as in all other cases, was obtained by the "differential" method.

Fig. III is the curve for magnesium chloride having a depth of 21 — 1 = 20 mm. and the corresponding water curve. The data from which these curves are plotted are given in Table III.

Fig. IV is the curve for magnesium chloride having a depth of 1 cm., also obtained by the "differential" method. These data are taken from Table IV.

Fig. V is the curve for aluminium sulphate having a depth of 21 — 1 = 20 mm. and the corresponding absorption curve for water.

Fig. VI is the curve for aluminium sulphate having a depth of 11 — 1 = 10 mm. and the corresponding water curve.

Fig. I shows the relative absorption of water and of the solution of calcium chloride having a concentration of 5.3 normal and a depth of 20 mm. The corresponding water curve is marked throughout by the symbol "H_2O." The solution is the more transparent from 0.9μ to nearly 1μ. The water then becomes the more transparent over a short region of wave lengths. From 1.05μ to 1.2μ the solution is

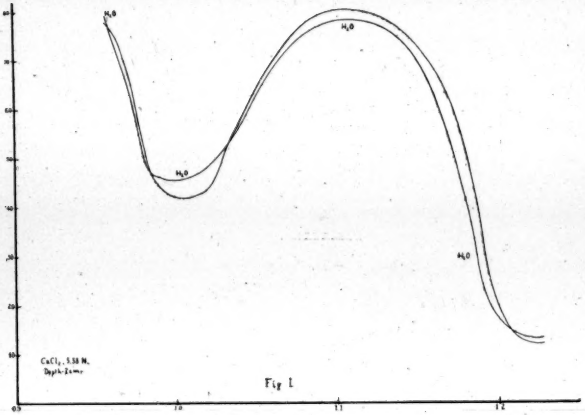

H_2O
H_2O
H_2O
H_2O
$CaCl_2$ 5.58 N.
Dept-1cm
1.0
1.1
1.2

Fig I

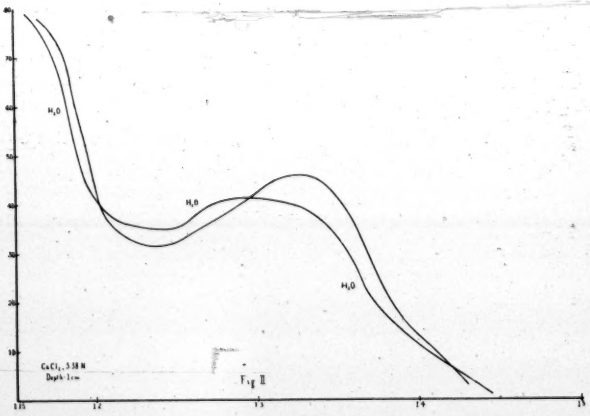

H_2O
H_2O
H_2O
$CaCl_2$ 5.58 N
Dept-1cm
1.2
1.3
1.4

Fig II

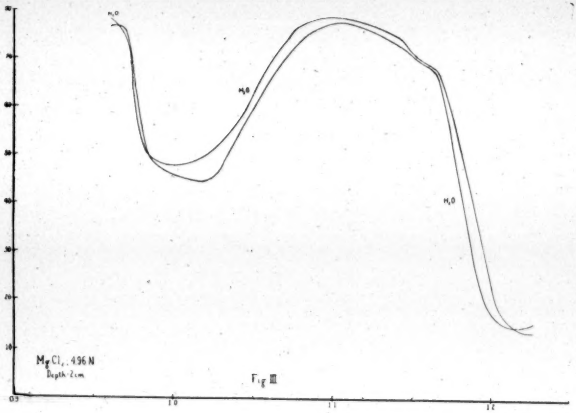


Fig III

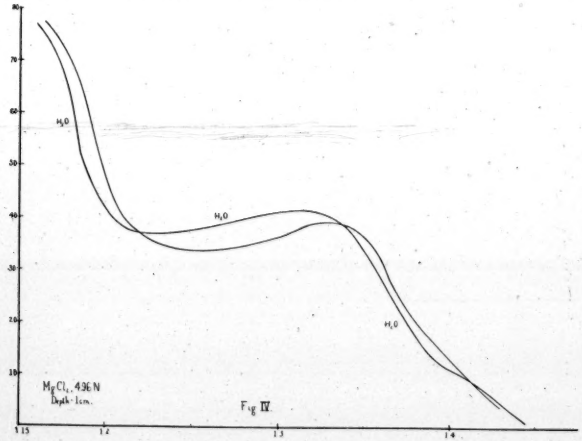


Fig IV

the more transparent. In this region the solution becomes as much as 25 per cent. more transparent than the pure water, as can be seen by comparing the points on the "water" curve with the corresponding points on the curve for the solutions which are vertically above the points on the water curve. The water becomes appreciably more transparent only at and near the bottom of the "water band" having a wave length of approximately 1μ. This is the effect that we would expect to get if the dissolved substance exerted a "damping" effect on the absorption of light by water.

It will be recalled that the salts which do not form hydrates show, in aqueous solution, practically the same absorption as the corresponding amount of water. It would, therefore, seem reasonable to account for the differences in the case of nonhydrating and strongly hydrating salts as due to the water of hydration, or the water that, in this case, is combined with the calcium chloride.

The curves in Fig. II are for a smaller depth of the same solution of calcium chloride. This figure brings out the same general relations as was shown in Fig. I. The water curve in the region 1.25μ is above that of the solution, showing that water in this region for the more shallow depth of solution is more transparent than the solution. The additional feature brought out by this figure is the water band in the region 1.4 to 1.5μ. After the first named water band is passed the solution becomes more transparent than the water, and remains so until the wave length 1.42μ is reached. Here both the solution and the water are practically opaque as is shown by both the curves approaching the abscissas.

The curve for magnesium chloride having a depth of 20 mm. is almost exactly a duplicate of that for calcium chloride having the same depth. Practically the only difference worthy of mention is in the region from 1.0μ to 1.1μ. In the case of magnesium chloride the water remains the more transparent over this region of wave lengths. In the case of calcium chloride the solution is the more transparent over this region. The difference in the transparency of the water and the solution throughout the region is, however, not very great. From

1.1μ towards the longer wave lengths, as we come down the descending arm of the curve towards the second water band, the water in the case of the magnesium chloride, as in the case of calcium chloride, becomes much more transparent than the solution, the differences here being of the same order of magnitude as those with calcium chloride.

Fig. IV gives the results for magnesium chloride with a depth of layer of 1 cm. The same relations hold in Fig. IV as in Fig. III, for the relative transparency of the water and of the solution. The water becomes the more transparent from 1.22μ to 1.34μ. For the longer wave lengths the solution becomes more transparent until the region 1.41μ is passed. For wave lengths longer than 1.41μ the transmission of both solution and water is practically zero, that is, they both become opaque to the longer wave lengths.

The results in Fig. V bring out some new features of interest and importance. These are the results that were obtained with aluminium sulphate. The new feature shown by the curve for aluminium sulphate, as compared with those for calcium chloride and magnesium chloride, is that at the minimum of the curve corresponding to wave length 1μ the solution is more transparent than the corresponding water. Beyond the wave length 1.04μ the water becomes the more transparent with aluminium sulphate as with magnesium chloride. Beyond the wave length 1.06μ the solution becomes more transparent in this case as with magnesium chloride and calcium chloride.

If we turn to Fig. VI the relations are as follows: In the region of 1.2μ the water is the more opaque. From 1.209μ to 1.306μ the water becomes the more transparent. From 1.306μ to the longest wave length studied, the solution again becomes more transparent than the corresponding layer of water.

An examination of all the results thus far obtained bearing on this problem leads us to conclude that the greater transparency of the solution as compared with the water in the solution must be due to some action of the dissolved sub-

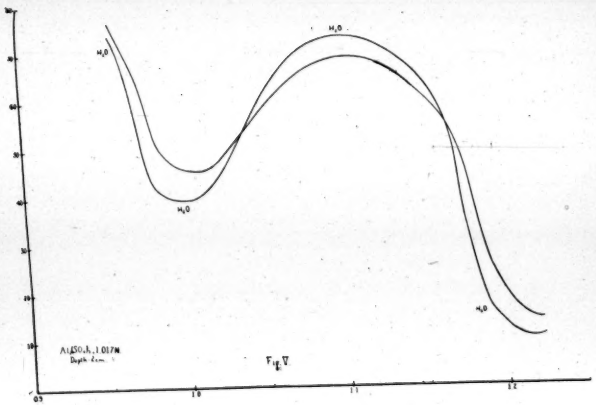

H₂O
H₂O
H₂O
H₂O
Al₂(SO₄)₃ 1.017N
Depth-cm.
1.0
1.1
1.2

Fig. V.

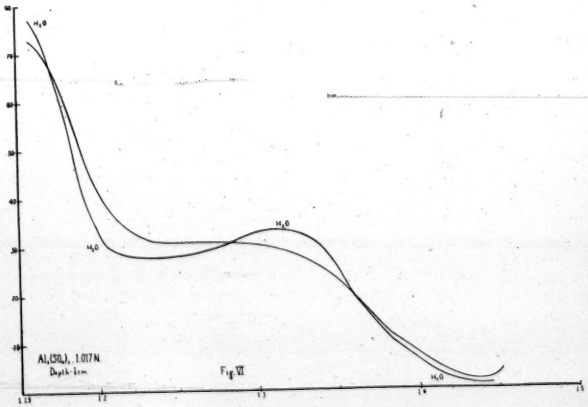

H₂O
H₂O
H₂O
H₂O
Al₂(SO₄)₃ 1.017N.
Depth-cm.
1.2
1.3
1.4

Fig. VI

stance on the solvent water. The question remains, what is this action?

We have seen from our earlier work on the absorption spectra of solutions, which has been in progress in this laboratory continuously for the past eight years, that the solvent can have a marked effect on the power of the dissolved substance to absorb light. This was first shown by Jones and Anderson,[1] and a large number of examples of this effect have since been found by Jones and Strong.[2] We interpreted the effect of the solvent on the power of the dissolved substance to absorb light as due to a combination between a part of the liquid present and the dissolved substance. This enabled us to explain a large number of facts that were brought to light for the first time by the investigations of the absorption spectra of solutions which have been carried on in this laboratory. Many of the phenomena which were thus explained, it seemed, could not be explained in terms of any other suggestion that has thus far been made. In a word, the solvate theory of solution, as proposed by Jones about a dozen years ago[3] to supplement the theory of electrolytic dissociation in order that we might have a theory of the real solutions which we use in the laboratory, and not simply a theory of ideal solutions as the theory of electrolytic dissociation alone must be regarded, has served good purpose in explaining the phenomena that have been previously observed in connection with the absorption of light by solutions of dissolved substances.

We are inclined to explain the phenomena recorded in this paper by means of the same theory. For solutions of those substances which have been shown by entirely different methods not to hydrate to any appreciable extent, the absorption of light by the solution and by a layer of water equal in depth to that of the water in the solution is, to within almost the limit of experimental error, the same.

For those substances which have been shown to form com-

[1] Carnegie Institution of Washington, Publication No. **110**.
[2] *Ibid.*, Nos. **130** and **160**.
[3] This Journal, **23**, 89 (1900).

plex hydrates, however, the absorption of light by their solutions and by a layer of water equal in depth to that of the water in the solution is very different. The water in these solutions is usually more opaque to light than the solution, or, what is the same thing in other words, a solution is more transparent than the water that is present in the solution.

The most rational explanation of this phenomenon appears to us to be that the part of the water that is combined with the dissolved substance has a smaller power to absorb light than pure, free, uncombined water. The fact that we are able to detect the difference between the water in the solution and pure water, by its action on light, we regard as good evidence in favor of the water in the solution being different from pure, free water. This difference, it seems to us, can be readily accounted for by the fact that a part of the water present in the solution is in combination with the dissolved substance.

We have carried out similar investigations with aluminium nitrate, but the concentration of the strongest solution that could be obtained was not sufficiently great to show the phenomenon in question. We, therefore, do not incorporate the results obtained with this substance. That the solutions must be very concentrated to show clearly the phenomenon with which we are dealing is shown by the results given in Table V. Here the solutions of the three salts in question that were used are more dilute than those for which the results are tabulated in Tables III and IV. An examination of this table will show that the phenomenon in question does not manifest itself to anything like the same extent as with the more concentrated solutions. This is exactly what we would expect in terms of the solvate theory of solutions. The more concentrated the solution the larger the total amount of the water present combined with the dissolved substance. If combination between water and the dissolved substance explains the facts recorded in this paper, then the larger the amount of water present that is combined with the dissolved substance, the more pronounced the phenomenon in question.

The results obtained with aluminium sulphate bring out the same facts shown by calcium chloride and magnesium

chloride. They, however, show in addition that water is more transparent in the region 1.1μ and more opaque at 1μ. That the sulphate should not agree throughout with the chlorides is really not surprising, since the sulphates show abnormal results in almost every particular. This is probably due, in part at least, to the large amount of polymerization which the sulphate molecules in general undergo in the presence of even water as a solvent. It should also be remembered in the present connection that, while calcium chloride and magnesium chloride crystallize with only six molecules of water, and are, therefore, only largely hydrated, aluminium sulphate crystallizes with 18 molecules of water and is, therefore, very largely hydrated.

The results in Table VI are, as has already been stated, the radiomicrometer deflections for a solution of aluminium sulphate and those for water having the same depth as the water in the solution in question, and the corresponding data for potassium chloride. A comparison of the two columns for potassium chloride and its corresponding water shows that the two are almost equally transparent to all the wave lengths studied.

A comparison of aluminium sulphate with its corresponding water brings out the phenomenon that we are now discussing in a very pronounced manner. It is for this reason that the data in this paper are given.

One other relation of a general character should be pointed out. The curves upon all six of the figures show that the addition of salt to water shifts the absorption towards the longer wave lengths. This is analogous to what has already been found by Jones and Uhler,[1] Jones and Anderson,[2] Jones and Strong,[3] and Guy and Jones,[4] when the absorption of salts as affected by the water present was studied. It was found that rise in temperature and increase in the concentration of the solution both tended to shift the absorption of the

[1] Carnegie Institution of Washington, Publication No. **60**.
[2] *Ibid.*, Publication No. **110**.
[3] *Ibid.*, Publications No. **130** and No. **160**.
[4] THIS JOURNAL, **49**, 1 (1913).

salt towards the longer wave lengths. The effect of rise in temperature and the increase in the concentration of the solution tended to simplify the hydrates in combination with the particles of the salt. The resonator within this simplified system seems to vibrate so as to shift the absorption bands towards the red.

The effect of the salt on the absorption of the water is the same as that of rise of temperature and increase of concentration on the absorption of the dissolved substance. We should naturally look for a similar explanation of the two sets of phenomena. It has been suggested by Dr. Guy that the effect of the salt on the absorption of light by water may be due to the breaking down of the associated molecules of water by the dissolved substance. This would be in keeping with the discovery made by Jones and Murray,[1] that one associated substance when dissolved in another associated substance diminishes its association.

In terms of this explanation, however, it is a little difficult to see why nonhydrated salts, such as were used in this work, do not also diminish the association of water and cause a shifting of its absorption bands towards the longer wave lengths. It may be that the effect of the dissolved substance in breaking down the association of the water is pronounced only in the case of water of hydration or the water that is combined with the dissolved substance, and that the explanation offered above is fundamentally correct.

In conclusion we wish to express our thanks to Professor A. H. Pfund, who has made many valuable suggestions during the progress of this work. We would also express our thanks to Dr. E. P. Wightman, who has kindly drawn the curves for us.

JOHNS HOPKINS UNIVERSITY
December, 1912

[1] THIS JOURNAL, **30**, 193 (1903).

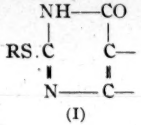
[Contributions from the Sheffield Laboratory of Yale University]

CCVII—RESEARCHES ON PYRIMIDINES
ALKYLATION WITH BENZYL CHLORIDE

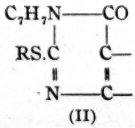
By Treat B. Johnson and Zai Ziang Zee

[SIXTIETH PAPER]

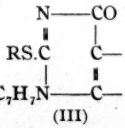
Every 2-mercapto-6-oxypyrimidine (I) which we have so far examined in this laboratory has undergone alkylation smoothly with benzyl chloride, in the presence of sodium ethylate, giving the corresponding N-benzyl derivatives, (II) or (III). In only one case have we observed the formation of an imido ester derivative corresponding to formula (IV).



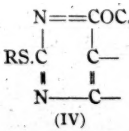
(I)



(II)



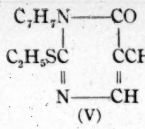
(III)



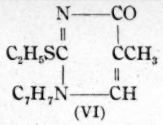
(IV)

2-Ethylmercapto-6-oxypyrimidine reacted with this halide, giving a mixture of the corresponding 1- and 3-benzylpyrimidines, while from 2-ethylmercapto-5-bromo-6-oxypyrimidine only a 3-benzyl derivative was isolated. The yield of this was, however, 60 per cent. of the theoretical.[1] From 2-ethylmercapto-5-methyl-6-oxypyrimidine[2] we obtained a yield of the N-benzylpyrimidines, (V) and (VI), corresponding to about 90 per cent. of the calculated amount, and 68 per cent. of this was the 3-benzylpyrimidine represented by formula (VI). Analogous results were obtained by alkylation of

[1] Johnson and Derby: This Journal, **40**, 444.
[2] Johnson and Derby: *Loc. cit.*

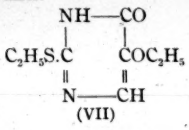


(V)

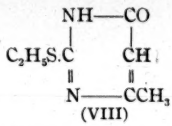


(VI)

2-ethylmercapto-5-ethoxy-6-oxypyrimidine[1] (VII), but 2-ethylmercapto-4-methyl-6-oxypyrimidine[2] (VIII) reacted abnormally. In the first case we obtained a mixture of the corresponding 1- and 3-benzyl derivatives, while with the second mercaptopyrimidine an inseparable mixture of the corresponding 1-benzyl-and 6-benzoxypyrimidines was obtained. The total yields of the alkylation products, in these two cases, were 94.0 and 87.5 per cent., respectively, of the calculated amounts.



(VII)



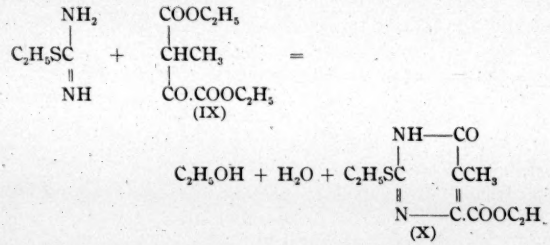
(VIII)

Therefore, in the case of methyl and ethylmercaptopyrimidines of Type (I), the substitution of a methyl group in positions 4 or 5 and a bromine atom or a negative ethoxy group in position 5 of the pyrimidine ring does not favor the formation of 6-benzoxypyrimidines (IV). The specific aim of the work described in this paper was to investigate the action of benzyl chloride on a 2-mercaptopyrimidine of Type (I), in which both positions 4 and 5 are substituted, and determine whether a strongly negative group functionating in position 4 of the ring would favor the formation of an oxygen substitution product (imido ester).

The pyrimidine which we selected for our investigation was ethyl 2-ethylmercapto-5-methyl-6-oxypyrimidine-4-carboxylate (X). This is easily prepared by condensation of pseudoethylthiourea with diethyl oxalopropionate[3] (IX), and has already been described in a previous paper from this labora-

[1] Johnson and Jones: THIS JOURNAL, **40**, 538.
[2] Wheeler and McFarland: *Ibid.*, **42**, 101.
[3] Arnold: Ann. Chem. (Liebig), **246**, 329, 336.

tory by Johnson and Mackenzie.[1] The condensation is represented as follows:



We now find that this pyrimidine (X) reacts smoothly with benzyl chloride in alcohol solution and in the presence of sodium ethylate, forming a benzyl derivative, in which the alkyl group is linked to the nitrogen occupying position 1 of the pyrimidine ring, viz., ethyl 1-benzyl-2-ethylmercapto-5-methyl-6-oxypyrimidine-4-carboxylate, represented by Formula (XIII). This pyrimidine is the chief product of the reaction; in fact, we were unable to isolate an isomeric 3-benzyl derivative in a pure condition. As regards a benzoxy derivative (XII), we obtained no evidence of its formation except the presence of a small amount of oil which contaminated the 1-benzylpyrimidine. Enough of this was, however, not obtained for further investigation.

That the product of our reaction was a 1-benzylpyrimidine (XIII) was established in the following manner: The mercapto compound, when digested with hydrochloric acid, underwent hydrolysis, with evolution of ethyl mercaptan and ethyl alcohol, forming quantitatively 1-benzyl-2,6-dioxy-5-methylpyrimidine-4-carboxylic acid (XIV). This acid was stable below its melting point, but when heated above this temperature (277°–279°) it underwent decomposition, with evolution of carbon dioxide, and was transformed smoothly into a benzylthymine melting at 203°–205°. This pyrimidine proved to be identical with 1-benzylthymine (XV), which

[1] This Journal, **42**, 368.

N—CO
C2H5SC CCH3
C7H7N—CCOOC2H5
(XI)
NH—CO
C2H5S.C CCH3
N—CCOOC2H5
(X)
N=—COC7H7
C2H5SC CCH3
N—CCOOC2H5
(XII)
C7H7N—CO
C2H5SC CCH3
N—CCOOC2H5
(XIII)
C7H7N—CO
CO CCH3
NH—CCOOH
(XIV)
C7H7N—CO
CO CCH3
NH—CH
(XV)
NH—CO
C2H5SC CCH3
N—CH
(XVI)
C7H7N—CO
C2H5SC CCH3
N—CH
(XVII)
C7H7N—CO
CO CCH3
NH—CCOOC2H5
(XVIII)

Johnson and Derby[1] obtained by hydrolysis of 1-benzyl-2-ethylmercapto-5-methyl-6-oxypyrimidine (XVII) with hydrochloric acid. An attempt to prepare ethyl 1-benzyl-2,6-dioxy-5-methylpyrimidine-4-carboxylate (XVIII) by alkylation of ethyl 2,6-dioxy-5-methylpyrimidine-4-carboxylate[2] with benzyl chloride was unsuccessful. The ester simply underwent saponification, by action of the alkali, and the corresponding acid[3] was formed. These various changes are represented by the above structural formulas.

Ethyl 2-ethylmercapto-5-methyl-6 - oxypyrimidine - 4 - carboxylate (X), therefore, reacts with benzyl chloride in the presence of alkali, and undergoes alkylation normally on a nitrogen atom, forming a 1-benzyl substitution product (XIII).

EXPERIMENTAL PART

Ethyl 2-Ethylmercapto-5-methyl-6-oxypyrimidine-4-carboxylate, $C_2H_5SC(NH{-}CO)=C(CH_3)-N{=}CCOOC_2H_5$.—This pyrimidine has been described in a previous paper from this laboratory.[4] It is obtained easily by condensation of pseudoethylthiourea with the sodium salt of diethyl oxalopropionate,

$$C_2H_5OOC.C(ONa) : C(CH_3)COOC_2H_5,$$

and crystallizes from alcohol in prismatic crystals which melt at 172°–173° to a clear oil.

Ethyl 2-Amino-5-methyl-6-oxypyrimidine-4-carboxylate, $H_2N.C(NH{-}CO)=C(CH_3)-N{=}CCOOC_2H_5$.—While the sodium salt of diethyl oxalopropionate condenses smoothly with either pseudomethyl- or pseudoethylthioureas, forming the corresponding mercaptopyrimidines, we were unable to obtain a good yield

[1] *Loc. cit.*
[2] Johnson: J. Biol. Chem., **3**, 299.
[3] Johnson: *Loc. cit.*
[4] Johnson and Mackenzie: THIS JOURNAL, **42**, 368.

of the above pyrimidine by condensation of this salt with guanidine. The sodium salt was prepared, as directed in our previous paper, by condensing 71.0 grams of diethyl oxalate with 50.0 grams of ethyl propionate in the presence of 11.5 grams of finely divided sodium. The salt was then dissolved in water with 58.0 grams of guanidine sulphocyanide and the solution combined with a strong aqueous solution of sodium hydroxide (20 grams). After allowing to stand for about 48 hours the solution was then acidified with hydrochloric acid, when this aminopyrimidine separated as a pink powder. The yield was small. This substance was difficultly soluble in cold water but separated from a hot solution in prismatic crystals which had no definite melting point. A nitrogen determination gave (Kjeldahl):

	Calculated for $C_8H_{11}N_3O_3$	Found
N	21.26	21.03

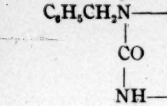
Action of Benzyl Chloride on Ethyl 2-Ethylmercapto-5-methyl-6-oxypyrimidine-4-carboxylate

Ethyl 1-Benzyl-2-ethylmercapto-5-methyl-6-oxypyrimidine-4-carboxylate, $C_2H_5S.C(=N-)CCH_3(=CCOOC_2H_5)$ $(-N=)CO-C_6H_5CH_2N$.—Four-tenths of a gram of sodium was dissolved in absolute alcohol, to which was then added 4.0 grams of ethyl 2-mercapto-5-methyl-6-oxypyrimidine-4-carboxylate and 2.1 grams of freshly distilled benzyl chloride. On warming sodium chloride began to separate at once and after heating a few hours (4–5 hours) on the steam bath the reaction was complete. The solution was then cooled, the sodium chloride separated by filtration and the alcohol filtrate concentrated to a small volume and then diluted with water. An oil deposited which solidified immediately after cooling. It was separated by filtration and dried on a porous plate to remove a trace of oily impurity which was present. The pyrimidine was extremely soluble in warm absolute alcohol and insoluble in

petroleum ether. It was purified by crystallization from alcohol and separated, on cooling, in colorless needles which melted at 69°–71° to a clear oil without effervescence. The yield of the purified pyrimidine was about 60.0 per cent. of the calculated. After concentration of the alcohol filtrates, more of the impure pyrimidine was obtained, but we were unable to isolate an isomeric benzyl derivative in pure condition. Analysis (Kjeldahl):

	Calculated for $C_{17}H_{30}O_3N_2S$	Found
N	8.43	8.50

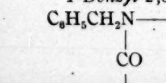
1-Benzyl-2,6-dioxy-5-methylpyrimidine-4-carboxylic Acid,



.—A quantitative yield of this pyrimidine was obtained by hydrolysis of the preceding pyrimidine with strong hydrochloric acid. It was insoluble in water and alcohol, but could be purified easily by crystallization from glacial acetic acid. It separated from this solvent in hexagonal tables which melted at 277°–279° with violent effervescence. It did not respond to a test for sulphur. A nitrogen determination gave (Kjeldahl):

	Calculated for $C_{13}H_{12}O_4N_2$	Found
N	10.80	11.1

1-Benzyl-2,6-dioxy-5-methylpyrimidine (*1-Benzylthymine*)



.—The above 1-benzyl-2,6-dioxy-5-methylpyrimidine-4-carboxylic acid was heated in a sulphuric acid bath at 285°–295° until effervescence ceased and all carbon dioxide was expelled. We obtained a dark oil, which solidified on cooling. This substance was then purified by crystallization from hot alcohol and separated, on cooling, in prismatic crystals which melted sharply at 203°–205° to a clear oil without effervescence. A mixture of this substance with

some 1-benzylthymine obtained in a previous investigation[1] melted at exactly the same temperature. Furthermore, the pyrimidine reacted with diazobenzenesulphonic acid, in the presence of sodium hydroxide, giving a characteristic purple solution. The yield was good. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{12}O_2N_2$	Found
N	12.96	12.9

An attempt to alkylate ethyl 2,6-dioxy-5-methylpyrimidine-4-carboxylate[2] with benzyl chloride in the presence of sodium ethylate was unsuccessful. One and five-tenths grams of the ester were digested in alcohol with the required amounts of sodium ethylate and benzyl chloride for 3 hours. The alcohol was then evaporated and the crystalline residue dissolved in water. On acidifying with hydrochloric acid we obtained 2,6-dioxy-5-methylpyrimidine-4-carboxylic acid,[2] which decomposed at about 325° with violent effervescence. The ester therefore simply underwent saponification by the above treatment and we obtained no evidence of the formation of a benzyl derivative. Analysis (Kjeldahl):

	Calculated for $C_6H_6O_4N_2$	Found
N	16.47	16.20

NEW HAVEN, CONN.
January, 13, 1913

ON THE PREPARATION AND PROPERTIES OF THE AMMONIUM SALTS OF SOME ORGANIC ACIDS[3]

BY LEROY MCMASTER

Most of the ammonium salts of organic acids described in the literature consist of a molecule of the ammonium salt combined with a molecule of the free acid in the case of monobasic acids, while, in the case of dibasic acids, the ammonium salt described is generally an acid ammonium salt. They were usually prepared by neutralizing an aqueouss solution of the acid with ammonia water or ammonium carbonate, and the

[1] Johnson and Derby: *Loc. cit.*
[2] Johnson: *Loc. cit.*
[3] Presented before the St. Louis Academy of Science, Feb. 17, 1913.

solution allowed to evaporate to crystallization. Many of the salts thus formed also contained water of crystallization.

In attempting to prepare some diammonium salts by the above method, Keiser and McMaster[1] always obtained the acid salts. They then dissolved the organic acids in absolute alcohol or ether and conducted into the solution a stream of dry ammonia gas. White crystalline salts were precipitated. In this manner they prepared the ammonium salts of fumaric, maleic, mesaconic and citraconic acids, which, upon analysis, proved to be the diammonium salts. Ammonium salts of malonic acid and *o*-phthalic acid were also prepared but were not analyzed.

I have continued this work on the dibasic acids, and have prepared the neutral ammonium salts of malonic, succinic, malic, tartaric, *o*-phthalic and *m*-phthalic acids. The method was applied also to the preparation of the ammonium salts of some monobasic acids—propionic, isobutyric, palmitic, benzoic and cinnamic. Some of the properties of these ammonium organic salts have also been studied. All of the acids used were obtained from Kahlbaum, except the tartaric acid, which was Baker's analyzed product.

Ammonium Malonate.—Finkelstein[2] attempted to make the neutral ammonium salt of malonic acid by adding an excess of ammonia water to an aqueous solution of the acid and allowing the mixture to evaporate over lime. The liquid lost ammonia and finally became acid. The acid ammonium salt crystallized out. I have prepared the neutral salt of malonic acid by the method described by Keiser and McMaster, but with some difficulty. If ammonia gas is conducted into an ethereal solution of the acid until no further precipitate is formed, the salt will be found not to be neutral. Analysis of two samples of the salt thus prepared gave respectively 16.65 per cent. and 16.62 per cent. of nitrogen. The acid ammonium salt of malonic acid contains 11.57 per cent. of nitrogen and the neutral salt 20.29 per cent. nitrogen. It is thus evident that each of these preparations was a mixture

[1] THIS JOURNAL, **49**, 84.

[2] Finkelstein: Ann. Chem. (Liebig), **133**, 338.

of the acid ammonium salt and the neutral salt. In this experiment dry ammonia was conducted into an ethereal solution of 5 grams of malonic acid for about one-half hour. However, if the ammonia is run into a solution of 5 grams of malonic acid for about three hours and allowed to come in contact with the precipitated salt, the neutral ammonium malonate is formed. The salt thus prepared is a white crystalline powder, not deliquescent but readily soluble in water. The aqueous solution is neutral. The salt, on analysis, gave the following results:

	Calculated for $CH_2(CO_2NH_4)_2$	Found I	Found II
N	20.29	20.3	20.26

The first nitrogen determination was made by the Dumas method, the second by the Kjeldahl method.

Ammoniun Succinate.—Berzelius states in his *Lehrbuch der Chemie* that the salt which results from the evaporation of a neutral solution of ammonium succinate is an acid salt. By adding an excess of ammonia to a solution of succinic acid and allowing the liquid to evaporate, Doepping[1] obtained a salt that was easily soluble in alcohol and not deliquescent. He concluded that he had a neutral salt. Fehling[2] found that the neutral salt could not be so easily prepared, and that the salt obtained by the method of neutralization and evaporation is either an acid salt or a mixture of the acid and neutral salts, especially if ammonia is used in excess. He obtained the neutral ammonium salt by adding to basic lead acetate an excess of a solution of neutral ammonium succinate and evaporating in a vacuum over sulphuric acid the mother liquor. As soon as the mass was mostly crystallized out, it was washed with a little water to remove traces of lead, pressed between filter paper and dried at 40°–50°. Fehling thus obtained the neutral ammonium succinate in crystalline form.

Dry ammonia gas was run into an alcoholic solution of succinic acid, and a white crystalline powder was formed which was not deliquescent in the air but dissolved readily in water.

[1] Doepping: Ann. Chem. (Liebig), **47**, 253.
[2] Fehling: *Ibid.*, **49**, 154.

The aqueous solution was neutral to sensitive litmus paper. The salt is only very slightly soluble in alcohol and was washed on the filter with alcohol and ether. The salt can also be prepared by conducting the ammonia into an ethereal solution of succinic acid.

The salt prepared in absolute alcohol gave, on analysis, the following results:

	Calculated for $(CH_2CO_2NH_4)_2$	Found I	Found II
N	18.42	18.36	18.38

Prepared in ether:

N	18.38

Ammonium Malate.—No record can be found of the preparation of neutral ammonium malate. The acid malates have been made and extensively studied by Pasteur[1] and Bremer.[2] When ammonia gas is run into an alcoholic solution of malic acid, there is first formed a white mucilaginous substance which soon changes to a crystalline powder. Analysis proved this salt to be a mixture of ammonium acid malate and the neutral malate. The neutral salt was prepared by passing the gas into a solution of 5 grams of the acid for several hours, the salt filtered off by suction, washed with alcohol and ether, dried in a desiccator, and then placed in a dry flask, filled with ammonia and tightly stoppered. The flask was shaken at intervals, and portions taken out from time to time and tested for neutrality. It was found necessary to allow the salt, prepared as described above, to stand in contact with the ammonia for three days in order to become neutral. The compound thus prepared was very slightly deliquescent and dissolved readily in water.

Determinations of nitrogen by the Kjeldahl method gave:

	Calculated for $C_4H_4O_5(NH_4)_2$	Found I	Found II
N	16.66	16.64	16.63

Ammonium Tartrate.—Tartaric acid was dissolved in absolute alcohol and ammonia gas passed into the solution until

[1] Pasteur: Ann. Chem. (Liebig), **82**, 331.
[2] Bremer: Ber. d. chem. Ges., **13**, 352.

a portion of the salt on being dissolved in water showed a neutral solution. When the ammonia was first passed in a white curdy precipitate formed. This soon changed to an amorphous powder which, as soon as neutral, was filtered by suction on an alundum crucible and washed with alcohol and ether. The salt is not at all deliquescent, and is very slightly soluble in alcohol.

Analysis gave the following result:

	Calculated for $C_4H_4O_6(NH_4)_2$	Found
N	15.21	15.19

Ammonium o-*Phthalate.*—Marignac[1] describes the preparation of this salt by the action of liquid ammonia on the acid. This salt was precipitated from an alcoholic solution of *o*-phthalic acid by dry ammonia, filtered by suction on an alundum crucible, washed with alcohol and ether, and dried in a desiccator. It is a fine white powder, soluble in water, scarcely soluble in alcohol. The salt is not deliquescent.

	Calculated for $C_6H_4(CO_2NH_4)_2$	Found
N	14.00	13.98

Ammonium m-*Phthalate.*—On passing ammonia gas into an alcoholic solution of *m*-phthalic acid a very voluminous, white, gelatinous precipitate was formed, which changed to a white powder. The salt was filtered by suction, and washed with only a small amount of alcohol, as it is somewhat soluble in this medium in the absence of the ammonia. The complete precipitation of this salt in alcohol depends, therefore, upon an excess of ammonia. Ammonium *o*-phthalate, on the other hand, is quite insoluble in alcohol. It was impossible to prepare ammonium *p*-phthalate by this method on account of the insolubility of *p*-phthalic acid in both alcohol and ether.

The ammonium *m*-phthalate was dried in a desiccator, and, on analysis, gave:

	Calculated for $C_6H_4(CO_2NH_4)_2$	Found
N	14.00	13.96

[1] Marignac: Ann. Chem. (Liebig), **42**, 215.

The method having proved so very applicable in the preparation of neutral ammonium salts of dibasic acids, it was next tried on the preparation of neutral ammonium salts of monobasic acids. Some work is in progress in this laboratory on the preparation of neutral salts of tribasic acids by the same method.

Ammonium Propionate.—When ammonia gas was first passed into an ethereal solution of propionic acid, no precipitate formed. White fumes came off which condensed in the top of the flask to a beautiful snow-white substance. After the gas was passed in for a short time, a white voluminous precipitate formed. The precipitate was quickly filtered by suction, washed with ether, placed in a vacuum desiccator for a few minutes and then in a calcium chloride desiccator. The salt deliquesces very readily, and is very soluble in water. On first dissolving the salt in water, the solution is neutral. The solution, however, soon turns acid, due to hydrolysis. The salt is very soluble in methyl alcohol, ethyl alcohol and acetic acid. Analysis proved it to be the neutral ammonium propionate.

	Calculated for $C_2H_5CO_2NH_4$	Found
N	15.38	15.4

Ammonium Isobutyrate.—Isobutyric acid was dissolved in ether, and ammonia passed into the solution. A snow-white precipitate of lustrous appearance formed. This was filtered by suction, washed with ether, and dried in a desiccator. Though not deliquescent, the salt cannot be dried in the air for it has a very high vapor tension. An appreciable quantity of the salt will disappear entirely in a short time if exposed to the air. The salt is soluble in alcohol and water. The aqueous solution is neutral.

Determination of nitrogen by the Kjeldahl method gave:

	Calculated for $C_4H_7O_2NH_4$	Found
N	13.33	13.32

Ammonium Benzoate.—By evaporating a solution of benzoic acid neutralized with ammonia there is obtained an acid salt

of the formula $NH_4C_7H_5O_2.C_7H_6O_2$ (Berzelius). The neutral salt can be obtained by conducting ammonia gas into an ethereal solution of benzoic acid. A white gelatinous precipitate was formed, which, after being filtered and washed with ether, dried in the air to an amorphous powder. It is not deliquescent, but soluble in water in which it shows a neutral reaction. The salt is somewhat soluble in ethyl alcohol, from which it can be crystallized. Analysis proved it to be the neutral ammonium benzoate.

	Calculated for $C_6H_5CO_2NH_4$	Found
N	11.02	11.02

Ammonium Cinnamate.—When ammonia gas was passed into an ethereal solution of cinnamic acid a white gelatinous precipitate at first formed which turned to an amorphous powder. It was necessary to pass the gas into the solution for several hours in order to obtain the neutral salt. The salt is soluble in water, and is not deliquescent in the air. If the salt is crystallized from alcohol, beautiful white crystals are formed which have a marked odor of oil of cinnamon. The original salt prepared in ether has no such odor. Also, the salt crystallized from alcohol is very much less soluble in water than the original salt. Ammonia was passed into an alcoholic solution of cinnamic acid, and there were formed at once glistening white crystals. After the ammonia was passed into the solution for some time, the alcohol was poured off from the crystals into a crystallizing dish and allowed to evaporate spontaneously. A further quantity of the crystals was obtained. These crystals, prepared from the alcoholic solution of the acid, had an odor of oil of cinnamon, but not so marked as in the case of the salt prepared in ethereal solution and afterwards crystallized from alcohol. The crystals prepared in alcohol were again found to be much less soluble in water than the amorphous powder prepared in ether.

Determination of nitrogen in the salt prepared in ether gave the result:

	Calculated for $C_9H_7O_2NH_4$	Found
N	8.48	8.49

Action of Ammonia on Palmitic Acid.—When dry ammonia gas was passed into an ethereal solution of palmitic acid there was produced at once a very voluminous, white gelatinous precipitate. The precipitate did not become crystalline even after passing in the gas for three hours. The precipitate was filtered by suction and washed with ether. It dried in the air to a white substance resembling a "soap." It was soluble in alcohol, especially if the alcohol was warm. Ammonia was also passed into an alcoholic solution of palmitic acid for three hours. No precipitate formed at first, but as the ammonia gas continued to pass into the solution a precipitate was formed which after a while dissolved and again after a short time reprecipitated. The precipitate and alcoholic solution were poured into a crystallizing dish and the alcohol allowed to evaporate. While wet with alcohol the precipitate was granular in appearance, but after the alcohol had entirely evaporated and the compound became dry, it had the appearance of the compound prepared in ether. The compound prepared in each case was evidently an ammonium "soap." It was not analyzed.

This investigation is being continued with other organic acids.

WASHINGTON UNIVERSITY
ST. LOUIS, MO.
Feb. 18, 1913

REPORTS

KETO-ENOL TAUTOMERISM

Quantitative Determination of Keto-Enol Tautomers

Until very recently, practically all quantitative determinations of the components of keto-enol tautomeric mixtures have been based on physical methods which, to be sure, are capable of great accuracy but the interpretation of which is generally uncertain. Of the chemical methods, that of Wislicenus,[1] based on the coloration of ferric chloride solutions produced by enol compounds, is limited to substances which rearrange very slowly, as ferric chloride not only disturbs the equilibrium but also increases catalytically the rearrangement velocity.

[1] Ann. Chem. (Liebig), **291**, 178 (1896). For a recent application of this method, see Knorr and Schubert: Ber. d. chem. Ges., **44**, 2772 (1911).

Claisen's method, depending on the solubility of enol compounds in dilute sodium carbonate solutions, can be applied only to substances in the solid state. The method proposed by Michael and Smith,[1] based on the action of tertiary bases, gives entirely erroneous results.

Of the physical methods, that based on the behavior towards electrical waves, which are absorbed only by hydroxyl compounds, is likewise unreliable.[2] The results obtained by the molecular rotation,[3] molecular refraction[4] and absorption methods[5] are trustworthy; the last method, which should prove especially valuable with substances which rearrange quickly, is limited, however, to solutions and in solvents which do not absorb light in the ultraviolet.

Kurt H. Meyer, of the Munich Academy of Sciences, has recently worked out a method which is extremely simple in operation, is applicable to either solids, liquids or solutions in any solvent and is apparently very accurate. By means of this method he has been able to make a large and very important contribution to our knowledge of keto-enol tautomeric compounds. The results of his investigation are published in a series of papers[6] which appeared during 1911 and 1912.

The method is based on the fact that all enols, which, of course, also contain a double bond, react instantly with bromine while all compounds which are unquestionably ketones do not. This difference is most marked in alcohol. In its simplest form, the determination is carried out as follows: The substance to be tested is quickly dissolved in alcohol and at once titrated with a standard solution of bromine in alcohol until the color of the bromine just persists after shaking. The reaction probably consists in the addition of bromine to the enol, $RR'C : C(OH)R''$, with formation of an unstable dibromide, $RR'CBrC(OH)BrR''$, which quickly loses hydrobromic acid, yielding a bromo ketone, $RR'CBrC(:O)R''$. Alcoholic solutions of bromine, however, are not stable and must be restandardized every time before using. Now the bromo ketones formed in the reaction are quantitatively reduced by hydriodic acid, on gentle warming in alcohol, to the ketone, with liberation of iodine which can be titrated with thiosulphate. Hydriodic acid probably adds to the bromo ketone,

[1] Ann. Chem. (Liebig), **363**, 36 (1908).

[2] Drude: Ber. d. chem. Ges., **30**, 940 (1897).

[3] Perkin: J. Chem. Soc., **61**, 800 (1892).

[4] Brühl: J. prakt. Chem., **50**, 119 (1894). See also Auwers: Ber. d. chem. Ges., **44**, 3525 (1911).

[5] Hantzsch: Ber. d. chem. Ges., **43**, 3049 (1910); **44**, 1771 (1911).

[6] Ann. Chem. (Liebig), **380**, 212, 220 (1911). Ber. d. chem. Ges., **44**, 2718, 2725, 2729 (1911); **45**, 2843, 2864 (1912).

while the bromine is replaced by iodine, a compound of the type RR′ClC(OH)IR″ being formed; such compounds, as shown by Finkelstein,[1] liberate iodine spontaneously:

$$RR'ClC(OH)IR'' \longrightarrow RR'C : C(OH)R'' + I_2$$

The substance to be tested, quickly dissolved in 50 cc. of 96 per cent. alcohol at about 10°, is treated at once with an approximately 0.1 N solution of bromine in alcohol (its exact concentration need not be known) in 0.5 cc. portions at a time and shaken after each addition until the color of the bromine persists about 2 seconds; the bromine is then decolorized with a few drops of thiosulphate solution, 5 cc. of a 5 per cent. solution of potassium iodide solution added, the mixture warmed gently and the iodine titrated to permanent decolorization with thiosulphate. It is best to prepare fresh bromine solutions before every determination, as old solutions influence the results of the titrations, probably owing to the formation of bromoacetaldehyde, which liberates iodine from hydriodic acid. The accuracy of the method may be judged from the following results obtained with artificially prepared mixtures of the pure enol and keto forms of acetyldibenzoylmethane:

Per cent. enol taken	100.0	45.5	28.04	37.85	25.0	68.70
Per cent. enol found	99.8	43.5	28.96	39.8	27.0	71.30

The addition of carbon tetrachloride or chloroform makes the end point somewhat less sharp, but does not influence the results. A large excess of alcohol must be present, however, and it is better, therefore, to use alcoholic solutions of bromine rather than the more stable chloroform solutions. If the ketone and enol are allowed to stand in alcohol, they will, of course, rearrange until equilibrium is established. After 12 hours, a 0.2 N solution of the originally pure ketone was found to contain 74.0 per cent. enol, that of the originally pure enol only 75.5 per cent., i. e., the same equilibrium point was reached, as was expected, from either the pure ketone or the pure enol side.

Tautomerism of Acetoacetic Ester

As this method of determination can be carried out very quickly, it seemed that it ought to be applicable to substances consisting of mixtures of labile tautomers, and Meyer undertook the investigation, by its means, of the ever-interesting problem of acetoacetic ester.

Solutions of the liquid ester in alcohol at —7°, titrated as described above, gave, as the result of determinations on 5

[1] Ber. d. chem. Ges., **43**, 1528 (1910).

solutions of different concentrations, 7.71, 7.71, 7.72, 7.70 and 7.75 per cent. enol. As the titration requires only 20-25 seconds, the error due to enolization during the determination is very slight; a solution allowed to stand 25 seconds after the end point had been reached absorbed about 0.2 cc. more of the bromine solution for each gram of ester. This error can be obviated by decolorizing the bromine with thiosulphate as soon as the end point is reached, adding 1–2 drops more of the thiosulphate, then the potassium iodide, and titrating back as before.

Experiments in solvents other than ethyl alcohol, viz., methyl, propyl and amyl alcohols, chloroform and water, gave the mean value 7.71 for the percentage of enol in the ordinary liquid ester. This value is thus seen to be independent of the nature of the solvent and of the concentration.

By applying the above method to solutions which have stood varying lengths of time, both the velocity of rearrangement and the equilibrium point can, of course, be determined. In solvents like hexane and carbon disulphide, the enol cannot be titrated directly, as the ester undergoes further bromination without a color change when the enol is used up; this difficulty can be obviated by diluting the solutions with a large volume of cold alcohol and titrating quickly. Below are given the percentages of enol at equilibrium in various solvents, together with the dielectric constants and association factors of the solvents:

Solvent	Per cent. enol	Dielec. const.	Assn. factor
Water	0.4	81.1	3.8
Glacial acetic acid	5.74	6.5	3.62
Methyl alcohol	6.87	35.4	3.43
Acetone	7.3	20.7	1.26
Liquid ester	7.71	....	....
Chloroform	8.2	5.2	....
Nitrobenzene	10.1	34.0	0.93
Ethyl alcohol	12.0	26.3	2.74
Ethyl acetate	12.9	6.1	
Benzene	16.2	2.25	
Ether	27.1	4.6	
Carbon disulphide	32.4	2.6	
Hexane	46.4	1.85	

As shown by the table, there is no relation between the amount of enol and the two series of constants for the solvents.

In *solution*, the amount of keto form increases with rise in temperature; thus, boiling solutions of the ester in methyl

and ethyl alcohol, when poured into much alcohol at —7° and titrated, gave only 4.74 and 7.50 per cent. enol, respectively. Heating the liquid ester alone, however, does not perceptibly change the equilibrium point, but distillation increases the amount of enol to 20–25 per cent.

Since the ratio of the concentrations, C_k/C_e, of the two forms at equilibrium in any given solvent is equal to the ratio of their solubilities, S_k/S_e, in that solvent, multiplied by some constant, K, independent of the solvent,[1] and since in a water solution of acetoacetic ester only 0.4 per cent. is present as enol, it seemed probable that the latter form would be much less soluble in water than the keto form. As a matter of fact, if a cold alkaline solution of the ester is acidified, an oil is precipitated which at once gives an intense color with ferric chloride and immediately decolorizes bromine. This oil is the free enol form but quickly rearranges into the keto form and redissolves. This isomerization is so rapid that a titration of the oil showed only 50 per cent. enol. Since in water the ester is present almost entirely as ketone, the solubility of the keto form may be taken as equal to that of the ordinary ester in that solvent (11.6 grams in 100 grams of solution at 0°). For the sake of comparison with the enol form, the solubility of the ordinary ester in 2 per cent. sodium chloride solution was also determined (10.9 grams in 100 grams solution). Again, since the enol form is precipitated from alkaline solutions by acids, its solubility in dilute sodium chloride solution can be approximately determined by preparing solutions of the ester of varying concentrations in dilute sodium hydroxide and noting which solution just becomes turbid on acidification with hydrochloric acid. In this way it was found that 0.5 gram of the enol dissolves in 100 grams of 2 per cent. sodium chloride solution. Knowing C_k, C_e, S_k and S_e, the constant K in the van't Hoff-Dimroth equation can be calculated. It comes out 0.09. In hexane, therefore, in which the ester, at equilibrium, contains 46 per cent. enol, the enol should be 9 times more soluble than the ketone form, and, as a matter of fact, by shaking the liquid ester with hexane, practically all the enol can be removed, leaving the almost pure ketone (98.5 per cent.).

Investigation of the rearrangement velocity of the ester by the bromine titration method gave the following values for the ketonization (K_k) and enolization (K_e) constants, respectively, at 0°:

[1] See Dimroth: Ann. Chem. (Liebig), **377**, 127 (1910).

Solvent	K_k	K^e
Liquid ester	0.00055	0.000046
Water	2.4	0.010
Alcohol (99.8 per cent.)	0.077	0.0105
Hexane	0.0041	0.0035

By Lapworth's method[1] (determination of the time required by the keto form to decolorize varying amounts of bromine), the value 0.013 was obtained for K_e in water at 0° and 0.039 at 10°. The somewhat higher value for 0°, as compared with that obtained by Meyer's method, is due to the fact that the hydrobromic acid formed in the Lapworth reaction catalyzes the rearrangement. Impurities, indeed, have marked catalytic effects, varying in magnitude with the nature of the solvent. In water and alcohol they are not so pronounced; the value for K_e in 0.1 N hydrochloric acid at 0° is 0.018. In nondissociating solvents, the influence of halogen acids is enormous; a few seconds after dissolving the ester in hexane or carbon disulphide containing hydrobromic acid, the percentages of enol were found to be 44.4–46.1 and 33.4, respectively. This probably explains why sharp end points in the bromine titration method are not obtained in these solvents, as hydrobromic acid is liberated in the reaction between the bromine and the enol. This catalytic effect of acids is apparently not due to hydrogen ions, since it is less marked in dissociating solvents. It is probably purely chemical, the acid adding to the ketone and then splitting off.

A short time after the appearance of Meyer's first two papers, Knorr, Rothe and Averbeck[2] published the results of an investigation in which they also succeeded in separating the two forms of the ester. They found that at the temperature of a carbon dioxide-ether mixture (—78°) the reversible transformation of the two forms of the ester into each other practically comes to a standstill and that the keto form is difficultly soluble in most solvents and can be crystallized from solvents which do not freeze at this temperature (alcohol, ether, hexane, ligroin, etc.) by cooling sufficiently concentrated solutions to —78°. In this way they obtained the keto form from ether or ether-alcohol mixtures in needles often 1–2 cm. long which, in a specially constructed apparatus from which all moisture was excluded, could be washed entirely free of the mother liquors containing the enol by means of low boiling (20°) ligroin or methyl ether. On drying in a high vacuum at —78°, the keto ester is obtained in perfectly pure condi-

[1] J. Chem. Soc., **85**, 30 (1904).
[2] Ber. d. chem. Ges., **44**, 1138 (1911).

tion. At —78° or in liquid air it is stable for a long time, and even at room temperature it requires weeks and months to reach the equilibrium point of the ordinary ester if catalytic influences are carefully excluded. In small quantities the ester can even be distilled in a vacuum without marked change. It boils at 40°–41° under 2 mm., solidifies sharply at —39° and its refractive index at 10° for the line *D* is 1.4225. It thus differs but slightly from the ordinary ester, which boils at 39°–40°, solidifies indefinitely at —45° to —43° and has the refractive index 1.4230–1.4232. At *room temperature*, according to the authors, it shows the same behavior towards ferric chloride as does the ordinary ester, but if equal amounts of the keto ester and the ordinary equilibrium mixture in various solvents at —78° are treated with equal amounts of ferric chloride in ether at —78° and then warmed up to —40° in the course of 2 minutes, markedly different periods of time are required for the appearance of the first faint red coloration, as shown in the following table:

Solvent	Equil. mixt.	Keto ester
Ether	Immediately	1 min. 20 sec.
Butyl alcohol	0 min. 6 sec.	.....
Propyl alcohol	0 min. 8 sec.	2 min. 0 sec.
Ethyl alcohol	0 min. 14 sec.	1 min. 20 sec.
Methyl alcohol	1 min. 20 sec.	1 min. 30 sec.

At —78° in alcohol, the reaction with the equilibrium mixture is perceptible in about 10 minutes, with the keto ester in only about 1.5 hours.

The isolation of the pure enol ester presented more difficulties. The sodium salt of the ester was treated, in small portions in suspension in petroleum ether (boiling below 20°) or methyl ether, with *not quite* the amount of hydrochloric acid gas necessary for complete decomposition of the salt, the sodium chloride filtered off, and the solution concentrated as quickly as possible at —78°, moisture being very carefully excluded. A specially constructed form of apparatus was used for these operations. The enol ester thus obtained is a colorless oil of strong, pleasant, fruity odor, solidifying in liquid air to a glassy mass which soon becomes crystalline. In very small quantities and in a very high vacuum, it can be distilled at about 33° without much change. Its refractive index at 10° for the line *D* is 1.4480. In ether-alcohol at —50°, it begins to show a red color with ferric chloride solution in 30–45 seconds, while the keto form under the same conditions requires 6 minutes 20 seconds.

By making artificial mixtures of the two pure forms and determining their refractive indices, a curve was constructed by means of which the composition of any mixture, and hence the composition at equilibrium and the velocity of rearrangement, could be determined. With the Abbé refractometer, only two drops of liquid are necessary for a determination. Using this method, the authors found that the ordinary equilibrium mixture of ester contains 2 per cent. enol, whereas Meyer, as shown above, obtained 7.71 per cent. Temperature does not appreciably affect the equilibrium. For the ketonization and enolization constants of the ordinary ester, they found 0.000172 and 0.00000376, respectively. The nature of the glass walls in which the determination is made has an enormous influence; the above values were obtained in a vessel which had been treated with hydrochloric acid, while in a new apparatus a value 100 times as large, viz., 0.0178, was obtained for $K_k + K_e$. Again, for a freshly distilled preparation of the enol ester, a still larger value, 0.613, for $K_k + K_e$ was found. Traces of both acids and bases, such as hydrochloric acid or tripropylamine fumes, cigarette smoke, contact with soft glass containing alkali, etc., exert a powerful catalytic influence on the ketonization. The authors observed that the percentage of enol in freshly distilled samples of the ordinary ester varies with the conditions of the distillation, the rapidity with which the hot vapors are condensed, etc. They also determined the percentage of enol at equilibrium in various solvents by concentrating the solutions at —78° and determining the refractive indices of the residues. They obtained the following values: In ether, 11 per cent. enol; in carbon disulphide, 25; in chloroform, 2; in petroleum ether, 27.5; in hexane, 31. These results, as will be seen, differ considerably from those obtained by Meyer.

Thus, although qualitatively Knorr's results agree with Meyer's, there are marked quantitative differences. The latter accordingly reinvestigated his method with a view to increasing its accuracy. In its simple form, it is subject to the following sources of error: The difficulty in determining the end point in the bromine titration; the rearrangement which may take place during the titration; the possibility that the alcoholic bromine solution may contain substances which liberate iodine from potassium iodide; and the possibility that the bromo ester formed may itself quickly react further with the bromine. The first two of these sources of error, which are the most serious, can be obviated by adding an excess of bromine and at once removing the excess. For this purpose a reagent must be used which reacts very rapidly with bro-

mine and not at all with iodine and whose reaction product with bromine is not affected by hydriodic acid. Such a substance is β-naphthol. Determinations by the modified method are carried out as follows: From 1–1.5 grams of the ester are quickly dissolved in 30 cc. of alcohol at —7°, enough 0.2–0.1 N alcoholic bromine solution to produce a yellow to brown color added at once, the mixture shaken and immediately treated with 2 cc. of a 10 per cent. β-naphthol solution until the bromine is decolorized. The whole operation requires but 15 seconds. Potassium iodide is now added and the solution is warmed and titrated with thiosulphate. As the mean of 7 determinations, the percentage of enol was found to be 7.51, with a maximum possible error due to isomerization during titration of 0.1–0.2 per cent. The true value may safely be taken as 7.4.[1] All the work reported in the earlier papers is likewise but slightly altered by the use of the modified method.

Applying his method to solutions increasing in dilution up to 0.2–0.1 N, Meyer made the surprising observation that the percentage of enol at equilibrium increases with the dilution, i. e., the equilibrium is not independent of the concentration. Below are given the results for the two extreme concentrations studied. The solutions were allowed to stand 3–4 days at room temperature in order to attain equilibrium. According to Meyer, the probable explanation is that even in the most dilute solutions studied the solvent is not "constant," i. e., it is not pure alcohol, benzene, etc., but a varying mixture of ester with alcohol, benzene, etc.:

Solvent	Conc. ester Per cent.	Per cent. Enol
Alcohol	65.0	7.8
Alcohol	1.0	13.2
Benzene	80.0	8.3
Benzene	2.1	20.6
Carbon disulphide	82.0	8.0
Carbon disulphide	0.9	39.2
Hexane	90.0	9.3
Hexane	1.7	58.6

The Ferric Chloride Reaction of Enols[2]

Just as the enol form of the ester can be determined by

[1] Auwers [Ber. d. chem. Ges., **44**, 3530 (1911)] recently obtained the value 9 per cent. by the refraction method.

[2] See Wislicenus: Ann. Chem. (Liebig), **291**, 172 (1896). Ber. d. chem. Ges., **32**, 2837 (1899). Hantzsch and Desch: Ann. Chem. (Liebig), **323**, 1 (1902). Stobbe: *Ibid.*, **352**, 132 (1907). Federlin: *Ibid.*, **356**, 251 (1907). Hantzsch: Ber. d. chem. Ges., **43**, 3068 (1910). Meyer: *Ibid.*, **44**, 2725 (1911). Knorr and Schubert: *Ibid.*, **44**, 2772 (1911).

titrating with bromine until the color of the bromine persists, so it can be determined in water in the presence of ferric chloride by adding bromine water quickly at 0° until the violet color of the iron enolate disappears. Experiments carried out in this way by Meyer showed that ferric chloride has an enolizing influence. The amount of enol at equilibrium depends upon the concentration of the ferric chloride but is not proportional to it. Probably part of the enol forms a complex with the ferric chloride and is not involved in the establishment of the equilibrium. In alcoholic solutions it is much more difficult to determine the amount of enolate formed on account of the indefiniteness of the end point and the great catalytic influence, in this solvent, of the ferric chloride on the rearrangement velocity. As is well known, the formation of the iron enolate is a slow process; by adding varying amounts of ferric chloride to an aqueous solution of the ester at 0° and determining the amount of enol formed after 5 minutes, Meyer found that the velocity of its formation is practically independent of the concentration of the ferric chloride. He concludes, therefore, that the formation of the enolate from the enol and ferric chloride is instantaneous and that the slow appearance of the color is due to the slow enolization of the keto form. In harmony with this view is the fact that if equal amounts of ester and ferric chloride are taken, the velocity curve obtained agrees well with that for a monomolecular reaction; the constant is 0.017, or approximately equal to that obtained for the rearrangement of the ester in 0.1 N hydrochloric acid, so that the catalytic effect of ferric chloride in water is about the same as that of free hydrochloric acid. As pointed out above, this catalytic influence is a serious objection to the use of the ferric chloride colorimetric methods for the determination of enols.

Desmotropy of Methyl Benzoylbenzoate

Meyer[1] and Knorr[2] simultaneously isolated the enol form of this ester. Both describe it as melting around 40° and Knorr gives the refractive index at 12°.5 for the line *D* as 1.5620, while that of the ordinary equilibrium mixture is 1.5418. Meyer finds by the bromine method that at equilibrium at room temperature the ordinary ester contains 16.7 per cent. enol; in glacial acetic acid at 20°, 14 per cent.; in alcohol, 21 per cent.; in carbon disulphide, 56 per cent.; in hexane, 69 per cent. The ketonization constant at 0° in alcohol is 0.10, the enolization constant 0.04. In boiling alcohol, the percentage

[1] Ber. d. chem. Ges., **44**, 2729 (1911).
[2] *Ibid.*, **44**, 2767 (1911).

of enol at equilibrium is 13.6. Unlike acetoacetic ester, however, the equilibrium point of methyl benzoylacetate is changed when the ester is heated without solvents; the percentage of enol decreases from 16.7 at 18° to 15.2 at 100° and 13.8–14.1 at 200°.

Relation between Constitution and Equilibrium in Keto-Enol Desmotropic Compounds

Having perfected his analytical method, Meyer now undertook a systematic study of a very large number of tautomeric keto-enol compounds. In this investigation he has made the following observations:

Homogeneously crystallized compounds are always homogeneous; equilibrium between keto-enol desmotropes never occurs in the crystalline state, only in the liquid and gaseous states and in solutions. No prediction can be made, from the structure of a solid, what its condition will be in solution. Thus, acetyldibenzoylmethane, which, in the solid state, has the keto form, is 90 per cent. enolized in alcohol, while the solid crystalline enolic methyl oxaloacetate is strongly ketonized in solution. This is brought out clearly in the following table:

Substance	Per cent. enol in cryst. solid	Per cent. enol at equil. in alcohol
Benzoylacetone	98	94
Dibenzoylmethane	96	90–100
β-Acetyldibenzoylmethane	2	90
Oxaloacetic acid	100	60
Benzoylacetic acid	98	40
Methyl oxaloacetate	100	23
Acetoacetanilide	1	18
Methylcyclohexanolonedicarboxylic ester	0	..

The percentages of enol at equilibrium in different tautomeric substances bear approximately the same ratio to each other in all solvents; in other words, if the percentages of enol in two substances are known in one solvent, the percentage of enol in one of them in any other solvent can be approximately calculated from the value for the other substance in that solvent. The following table gives the ratio *enol : ketone* of three tautomeric substances in various solvents. As this table shows, the relative amounts of enol in acetylacetone are, in all solvents, 30–50 times greater and those in methyl benzoylacetate about 2.2 times greater than in acetoacetic ester:

Solvent	Acetoacetic ester	Methyl benzoyl-acetate	Acetyl-acetone
Water	0.004	0.008	0.24
Formic acid	0.011	0.028	0.9
Glacial acetic acid	0.061	0.16	2.8
Methyl alcohol	0.074	0.16	2.6
Liquid tautomers	0.079	0.20	3.2
Chloroform	0.089	0.19	3.8
Ethyl alcohol	0.15	0.35	5.3
Benzene	0.22	0.45	5.7
Hexane	0.9	2.2	12.0

Compounds with One C(: O)R Group.—Such substances as acetaldehyde, acetone, acetophenone and pyroracemic acid contain no enol, even in alcoholic solution in the presence of sodium ethylate.

Compounds with Two C(: O)R Groups.—If, in compounds of this type, $R(O :)CCH_2C(: O)R'$, $R(O :)CCH_2$ is kept the same and C(: O)R′ is varied, it is found that the percentage of enol at equilibrium increases in the order $C(: O)R' = COOCH_3$, $COOC_2H_5$, COOH, $CONHC_6H_5$, $CO.CH_3$, $CO.C_6H_5$, $COCOOR''$, as shown by the following table:

Substance	Per cent. enol in Liquid tautomer	Alcohol
$H_3COOCCH_2$ combined with:		
$COOCH_3$	0	0
$CO.CH_3$	4.8	12.6
$CO.C_6H_5$	16.7	26.0
$COCOOCH_3$	100.0 (solid)	23.0(?)
$H_5C_2OOCCH_2$ combined with:		
$COOC_2H_5$	0	0
$CO.CH_3$	7.4	13.0
$CO.C_6H_5$	29.2	27.0
$COCOOC_2H_5$	88.0	50.0
$HOOCCH_2$ combined with:		
COOH	0	0
$CO.C_6H_5$	100.0 (solid)	40.0
COCOOH	100.0 (solid)	60.0
$H_3C.OCCH_2$ combined with:		
$COOCH_3$	4.8	12.6
$COOC_2H_5$	7.4	13.0
$CONHC_6H_5$	0 (solid)	18.0
$CO.CH_3$	76.0	84.0
$CO.C_6H_5$	100.0 (solid)	94.0

$H_5C_6.OCCH_2$ combined with:		
$COOCH_3$	16.7	26.0
$COOC_2H_5$	29.2	27.0
$COOH$	100.0 (solid)	40.0
$CO.CH_3$	100.0 (solid)	94.0
$CO.C_6H_5$	100.0 (solid)	90–100
$R''OOCCOCH_2$ combined with:		
$COOCH_3$	100.0 (solid)	23.0
$COOC_2H_5$	88.0	50.0
$COOH$	100.0 (solid)	60.0

The enolizing tendency of the group $C(:O)H$, i. e., $R' = H$, was studied in only one case., viz., that of formylphenylacetic ester, $H_5C_2OOCCH_2C(:O)H$, which contains about 76 per cent. enol in the liquid state and 20–25 per cent. in alcohol.

If the acids, $HOC(:O)R'$, from which are derived the groups $C(:O)R'$, whose enolizing tendency has been determined as above, are arranged in order of increasing dissociation constants, as shown below, it will be seen that they fall into the same order as their derived groups arranged in order of increasing enolizing tendency.

Acid		Dissoc. const. $K = 100k$
$HOCOOCH_3$	Monomethyl carbonate	.....
$HOCOH$	Carbonic	0.00001
$HOCO.CH_3$	Acetic	0.0018
$HOCO.C_6H_5$	Benzoic	0.007
$HOCO.H$	Formic	0.021
$HOCOCOOH$	Oxalic	About 10.0

Compounds with Three Substituents.—No general relation can be established between the constitution of compounds of this type, $R(O:)CCHR''C(:O)R'$, and the percentage of enol they contain at equilibrium. When R'' is an alkyl the enol content is generally lower than when R'' is a hydrogen atom. If R'' is an acyl group, however, the enolization is generally increased if the unsubstituted compound itself is only slightly enolized; otherwise it is decreased. The results with this class of compounds are summarized below:

Substance $R'' = H$	Per cent. enol in liquid
$CH_3COCH_2COOCH_3$	4.8
$CH_3COCH_2COOC_2H_5$	7.4
$C_6H_5COCH_2COOC_2H_5$	29.2
$CH_3COCH_2COCH_3$	76.0
$H_5C_2OOCCH_2COOC_2H_5$	0
$CH_3COCH_2COOC_2H_5$	7.4
$C_6H_5COCH_2COCH_3$	enol stable

Substance	Per cent. enol in liquid
R' = alkyl	
$CH_3COCH(CH_3)COOCH_3$	3.0
$CH_3COCH(C_2H_5)COOC_2H_5$	3.1
$CH_3COCH(CH_2C_6H_5)COOC_2H_5$	5.0
$CH_3COCH(CH_2COOC_2H_5)COOC_2H_5$	3.7
$C_6H_5COCH(CH_2COOC_2H_5)COOC_2H_5$	4.1
$CH_3COCH(CH_3)COCH_3$	30.0
R' = acyl	
$H_5C_2OOCCH(COOC_2H_5)COOC_2H_5$	0.2
$H_5C_2OOCCH(COCH_3)COOC_2H_5$	64.0
$CH_3COCH(COCH_3)COOC_2H_5$	90–100
$CH_3COCH(COC_6H_5)COOC_2H_5$	60.0
$C_6H_5COCH(COOC_2H_5)COCH_3$	60.0
$C_6H_5COCH(COC_6H_5)COCH_3$	ketone stable

Desmotropy of Malonic Ester and Methanetricarboxylic Ester

Free malonic ester contains at most 0.01 per cent. enol, but if a solution in methyl alcoholic sodium methylate is poured directly into a strongly cooled, acidified solution of bromine in methyl alcohol so that the enol can be brominated at the instant that it is formed, as much as 50 per cent. enol can be detected.

Crystalline methanetricarboxylic ester is pure ketone; the liquid ester contains 0.2 per cent. enol; when liberated from its sodium methylate solution as described above for the malonic ester, 75–87 per cent. enol can be detected.

By these experiments Meyer has shown that ester groups can exhibit desmotropy just as well as ketone groups:

$$CHCOOR \rightleftarrows C : C(OH)R$$

C. A. R.

MOLECULARLY ASYMMETRIC METALLIC COMPOUNDS[1]

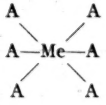
Gentlemen, permit me, first, to extend my sincere thanks to your President for the honor which he has done me in inviting me to lay before you the results of our investigations on molecularly asymmetric metallic compounds. These studies may be considered as a continuation of the investigations begun by one of your most famous countrymen, by Pasteur, and I could not better begin my report than by expressing the great satisfaction I feel in having been able to widen, to a

[1] Address by Prof. A. Werner, of the University of Zurich, delivered before the Chemical Society of France on May 24, 1912, and published in the Bull. soc. chim., for July 20, 1912.

small extent, the field of the application of his great principle of molecular asymmetry and to continue the work of Le Bel and van't Hoff.

Gentlemen, the hypotheses on the arrangement in space of the atoms of the molecules of carbon compounds did not take a precise form until the tetravalence of carbon was clearly established. It was, in fact, only after this fundamental principle in the structure of organic molecules had been revealed and it had led to a general point of view and a classification of organic compounds, that it was possible to take up the question of the arrangement in space of the four groups which are combined with the carbon atom and to explain certain phenomena of isomerism by means of considerations on the different arrangement in space of these four groups.

The development of the theoretical conceptions relative to the stereochemical formulas of inorganic compounds followed an entirely analogous course. It was seen first that a large number of elementary metallic atoms have the property of forming complex radicals, MeA_6, in which the metallic atom Me is combined directly with the six groups A, so that these complex radicals must correspond to the structural formula



The exactitude of this structural formula was established as the result of numerous investigations on the number of ions which the complex inorganic compounds form in aqueous solutions, investigations based especially on the determinations of the electrolytic conductivity of aqueous solutions of these compounds, for the groups directly combined with the central atom remain combined with the latter when the compounds are dissolved in water and consequently take no part in the electrolytic conductivity and do not appear in the form of ions free and independent of the central atom.

A new decisive experimental proof of the structural formula of these complex radicals was furnished by the discovery of a great number of new isomerism phenomena, predicted by the theory, as, for example, coördination polymerism, coördination isomerism, ionization metamerism, hydration isomerism, salt isomerism, isomerism phenomena, of which I had the honor to speak to you, some years ago, in an address made in Haller's laboratory. Thanks to these investigations on the con-

stitution of complex inorganic compounds, the important conception of the coördination index of elements was acquired, a conception which may now be summarized as follows: The coördination index of a large number of elementary atoms is equal to six, i. e., they have the power of combining with six other atoms.

We cannot take up here the nature of the forces which unite the six groups to the central atom; we shall note only that the affinity brought into play may manifest itself either in the form of principal valences or in the form of secondary valences.

As examples of compounds containing a complex radical, MeA_6, we may cite the following:

$[Co(NO_2)_6]R_3$, $[PtCl_6]R_2$, $[AlF_6]Na_3$, $[Fe(CN)_6]R_4$, $[Co(NH_3)_6]X_3$,

$Pt\begin{matrix}(NH_3)_2\\Cl_4\end{matrix}$, $\left[Pt\begin{matrix}NH_3\\Cl_5\end{matrix}\right]R$, $[Cr(OH_2)_6]X_3$, $\left[\begin{matrix}OH\\NO\end{matrix}Ru(NH_3)_4\right]X_2$, etc.

The number of compounds containing a radical of this type is very large.

Just as in the discussion of stereochemical problems relating to organic compounds the structural formula, CH_4, of methane serves as basis, so the structural formula, MeA_6, of the complex radicals serves as basis for the study of the configuration in space of inorganic molecules.

The first principal extension of our knowledge of the constitution of the complex radicals MeA_6 was gained experimentally and led to the admission that the six coördination positions of the central elementary atom are equivalent. This conception is derived from the impossibility of preparing isomeric compounds containing complex radicals, $Me\begin{matrix}A_5\\B\end{matrix}$. We conclude that in the radicals MeA_6, the arrangement of the six groups around the central atom is symmetrical.

Theoretically, three different symmetrical arrangements can be imagined—the plane, the prismatic and the octahedral arrangement.

With the first two of these arrangements we can conceive of three series of isomers of compounds with the complex radicals $Me\begin{matrix}A_4\\B_2\end{matrix}$; the octahedral arrangement, on the other hand, demands but two. Here again, it was experimental investigation which served to answer the question as to which of the arrangements mentioned corresponds to the configuration of

these complex radicals. By means of numerous researches, it has been possible to show that there are never three series of isomers, but only two, and there are now known for the compounds of cobalt about 30 types of compounds with the complex radicals $Me^{A_4}_{B_2}$ which exist in the form of two series of stereochemical isomers; similar compounds of chromium and platinum are known.

We can conclude with certainty that the six groups occupy the octahedral arrangement around the central atom. The problem of the determination of the configuration formulas of the isomers, i. e., of the determination of the relative positions occupied in the octahedral arrangement by the groups B of the isomeric radicals $Me^{A_4}_{B_2}$, has likewise been solved in a satisfactory manner.

The configuration formulas deduced for the octahedral arrangement for the isomers with the complex radicals $Me^{A_4}_{B_2}$ contain the two groups B in different and opposite positions; in one of the forms they are in a near (*cis*) position and in the other in a distant (*trans*) position.

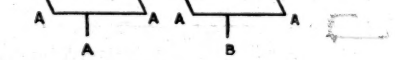


Fig. 1

These stereochemical formulas show, therefore, differences analogous to those of the formulas of maleic and fumaric acids, and we could therefore expect differences in properties between the inorganic stereochemical isomers analogous to those found between maleic and fumaric acids. It has been possible to verify experimentally these theoretical previsions. Of the two series of stereochemical isomers, only one shows direct relations with compounds containing in the place of the two groups B a radical forming a closed chain with the central atom, from which we may conclude that only in this series of isomers are the two groups B in a near (*cis*) position, i. e., in a position favorable for the closing of the chain.

With the experimental sanction of these relations and others, it has been possible to determine the configuration formulas of all the isomeric series, and the configurations thus established have been confirmed by the researches on optical isomers, with which their study is related. From the octahedral formula, in fact, we can predict, besides the stereochemical isomers already mentioned, others which belong to the group of isomers with nonsuperposable images, and by the experimental confirmation of these extreme conclusions a new decisive proof for the octahedral formula was obtained, for these phenomena of optical isomerism can neither be foreseen nor explained by any other theoretical conception. Let us first take up briefly the theoretical conclusions deduced from the octahedral arrangement.

The octahedral arrangement leads, for a number of inorganic complex compounds, to configuration formulas with nonsuperposable images. I should like, however, to limit my theoretical conclusions to simple cases easily attacked experimentally. Cases of this kind are found among compounds with the complex radicals $Me\begin{matrix}A_4\\B_2\end{matrix}$, i. e., among the compounds which we have already taken up in our development of stereochemical isomerism. When the composition of the complex radicals $Me\begin{matrix}A_4\\B_2\end{matrix}$ is such that 2 coördinately bivalent groups, such as ethylenediamine or other groups of analogous constitution, are substituted for the four groups A, and the two groups B are in the near (*cis*) position, the space formulas of these compounds are not superposable on their images. We may distinguish three different cases:

a. Compounds with complex radicals $\left[\begin{matrix}A\\B\end{matrix}MeEn_2\right]$. These complex radicals contain two asymmetric tetrahedrons (A, B, En, Me) which, as the result of the different orientation in space of the two molecules of ethylenediamine (En), are not identical.

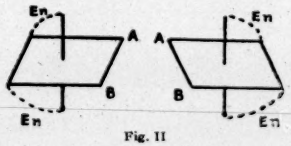


Fig. II

b. Compounds with complex radicals $\left[\begin{matrix}B\\B\end{matrix}MeEn_2\right]$. These complex radicals contain no asymmetric tetrahedral grouping. We therefore have there a kind of molecular asymmetry which we shall designate by the expression "molecular asymmetry I."

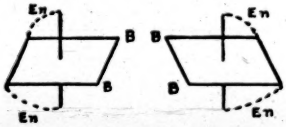


Fig. III

c. Compounds with complex radicals $[MeEn_3]X_3$. These complex radicals contain three equal, coördinately bivalent groups. We shall call this asymmetry "molecular asymmetry II."

Fig. IV

The stereochemical formulas of the *trans* isomers of all these compounds are superposable on their images and consequently we can expect no optical isomerism for these compounds.

The results of our researches harmonize perfectly with these theoretical deductions. We have been able to resolve into their optically active modifications the *cis* forms of the compounds of all the formula-types indicated above, but all efforts to resolve the *trans* isomers were unsuccessful. We may note, further, that in all cases the two active modifications have equal and opposite rotatory powers.

I shall point out now, in what follows, how these resolutions have been effected in practice and what the properties of the optical isomers are.

Methods of Resolution

Thus far, we have not employed in our researches the spontaneous and biochemical methods of resolution; we have

limited ourselves to the method generally employed in organic chemistry for the resolution of active bases. We caused the halogen salts of the series to be resolved to react with the silver salts of optically active acids, and then separated into their components, by means of fractional crystallization, the mixtures of salts formed. Among the acids which were used, we may mention especially the α-bromocamphorsulphonic acids and Reychler's camphorsulphonic acids.

The α-bromocamphorsulphonic acids are much preferable to the camphorsulphonic acids, for thus far we have been able to resolve only two series of compounds by means of the camphorsulphonates, while we have resolved eight of them with the bromocamphorsulphonates.

Nevertheless, α-bromocamphorsulphonic acid is not a general agent for the resolution, for we have found that different series form partial racemates, so that the resolution is not successful. This, for example, is the case in the 1,2-diamminediethylenediaminecobaltic and the carbonatodiethylenediaminecobaltic series and others.

As regards the resolution by means of the *d*-α-bromocamphorsulphonic and *d*-camphorsulphonic salts, it should be noted that the isolation of the active series forming slightly soluble salts is easy, but the purification of the sometimes exceedingly soluble salts of the series of opposite rotatory power often presents difficulties. To get around these difficulties, we have, in certain cases, retransformed the soluble sulphonates into halogen salts and caused these to react with the *l*-bromocamphorsulphonate or camphorsulphonate of silver, so as to obtain difficultly soluble salts of the series of opposite rotatory power. By this method we have been able to isolate quantitatively the optical isomers.

In certain cases, the *l*-bromocamphorsulphonic acid, which is difficultly accessible, can be replaced by *d*-camphorsulphonic acid, for the solubility of the camphorsulphonates is often the inverse of that of the corresponding α-bromocamphorsulphonates. It is possible, therefore, in preparing the *d*-camphorsulphonate, to first isolate one of the series, then, starting with the salts remaining in the mother liquor, to prepare the *d*-camphorsulphonate of the opposite series. It goes without saying that the order of preparation of the bromocamphorsulphonates and camphorsulphonates can be reversed.

We likewise made numerous attempts to resolve the tartrates of different series by subjecting them to fractional crystallizations, but the results obtained were not satisfactory. On the other hand, we were able to determine that the resolution compounds with trivalent radicals, corresponding

to the general formula $[MeEn_3]X_3$, can be effected with remarkable success by means of mixed salts, such as the chloride tartrates and bromide tartrates,

$$[MeEn_3]^{Cl}_{C_4H_4O_6} \quad \text{and} \quad [MeEn_3]^{Br}_{C_4H_4O_6}$$

which do not form partial racemates.

The method of fractional crystallization which we have just described has rendered us great service, but as it involves crystallizations in aqueous solutions it is applicable only to the case of compounds stable in aqueous solution. Therefore compounds with complex radicals containing groups which, by the action of water, are easily dissociated into the form of ions are almost excluded from this method. It is thus that the resolution of the 1,2-chloronitrodiethylenediaminecobaltic salts was effected only with a very great loss of product.

To overcome these difficulties, we devised a method which is applicable to cases where the differences of solubility between the bromocamphorsulphonates or camphorsulphonates of the optical isomers are very large.

This method has, on the one hand, the advantage of not requiring the silver salts of the active acids, which, when the complex radicals contain a halogen, may give rise to secondary reactions, and furthermore avoids a long standing of the salts to be resolved in the aqueous solution, which is quite important in the cases where these salts are easily altered by water. The new method is based on a simple precipitation process. If active ammonium bromocamphorsulphonate is added to a concentrated solution of the racemic compound to be resolved, one of whose active components gives a difficultly soluble bromocamphorsulphonate, the latter is precipitated, in some cases in pure state, in others mixed with a little of the partial racemate. (In the latter case, the precipitated salt is transformed into an easily soluble salt and its solution is again precipitated with ammonium bromocamphorsulphonate.) From the mother liquors from the first precipitation, the series with opposite rotatory power can be isolated by adding the isomeric active ammonium bromocamphorsulphonate. By means of this method, it has been possible to resolve the *cis*-dichlorodiethylenediaminecobaltic series, which, in aqueous solution, is very rapidly transformed into the chloroaquocobaltic series. But the best results have been obtained in the *cis*-chloroisosulphocyanodiethylenediaminecobaltic series, because the *d*-bromocamphorsulphonate of the *l*-rotatory form

and the *l*-bromocamphorsulphonate of the *d*-rotatory form of this series are almost insoluble in water. The importance of the new method has been increased lately by the use of the sodium salt of nitrocamphor, which we shall call sodium camphornitronate. This compound has made possible the resolution of series which could not be resolved by means of the bromocamphorsulphonates and camphorsulphonates. The method of using sodium camphornitronate is the same as that for the ammonium salts of camphor- and bromocamphorsulphonic acids. Likewise, ammonium tartrate has rendered services in one case where the other methods did not succeed. We have found that, for the resolution of irontri-α-dipyridyl, ammonium tartrate can be used in the same way as ammonium camphorsulphonate, ammonium bromocamphorsulphonate and sodium camphornitronate in the other cases.

Summarizing the new points of view bearing on the resolution of inorganic racemic compounds which result from our investigations, we reach the following conclusions:

1. Certain mixed salts, i. e., salts which, besides radicals of active acids, also contain radicals of inactive acids, such as the chloride-tartrates and bromide-tartrates, lend themselves in a peculiar manner to the resolution by fractional crystallization of racemic inorganic compounds.

2. Instead of the method of resolution generally used in organic chemistry, which is based on fractional crystallization and which is often inapplicable to inorganic compounds, advantageous use can be made of a new method, which consists in precipitating one of the active components from the aqueous solution of the racemate by means of the soluble salts of active acids.

General Summary of Active Metallic Compounds

Let us pass now to a general summary of the active metallic compounds thus far obtained. By fractional crystallization, the following series of metallic compounds have been resolved into their active modifications:

1. 1,2-Chloroamminediethylenediaminecobaltic series.
2. 1,2-Bromoamminediethylenediaminecobaltic series.
3. Tetraethylenediamine-μ-aminoperoxodicobaltic series.
4. Tetraethylenediamine-μ-aminonitrodicobaltic series.

The resolution of these four series was effected with the bromocamphorsulphonates. The 1,2-dinitrodiethylenediaminecobaltic series was resolved by means of the bromocamphorsulphonates and the camphorsulphonates. For the tri-

ethylenediaminecobaltic and triethylenediaminerhodic series, the resolution succeeded with the chloride-tartrates; for the triethylenediaminecobaltic series, with the bromide-tartrates also.

By precipitation of concentrated solutions of racemates with ammonium *d*-bromocamphorsulphonate, we have been able to obtain the difficultly soluble bromocamphorsulphonates of the following series:

1. *d*-Chloroamminediethylenediaminecobaltic series.
2. *d*-Bromoamminediethylenediaminecobaltic series.
3. 1,2-*l*-Dichlorodiethylenediaminecobaltic series.
4. *d*-Chloronitrodiethylenediaminecobaltic series.
5. *l*-Chloroisosulphocyanodiethylenediaminecobaltic series.
6. *l*-Dichlorodiethylenediaminechromic series.

With ammonium *d*-camphorsulphonate, we were able to precipitate the *l*-chloronitrodiethylenediaminecobaltic and *l*-bromonitrodiethylenediaminecobaltic camphorsulphonates; finally, with ammonium *d*-tartrate, the tartrate of *l*-rotatory irontri-β-dipyridyl; and with sodium camphornitronate, the *d*-triethylenediaminechromic and *l*-triethylenediaminerhodic camphornitronates.

Let us add to this enumeration the active metallic compounds prepared by chemical reactions from active compounds obtained by resolution. They are the following:

$$\left[\begin{matrix}H_2O\\H_3N\end{matrix}\!\!>\!CoEn_2\right]X_3,\quad \left[\begin{matrix}H_3N\\H_3N\end{matrix}\!\!>\!CoEn_2\right]X_3,$$

$$\left[OC\begin{matrix}O.\\O.\end{matrix}\!\!>\!CoEn_2\right]X,\quad \left[\begin{matrix}O_2N\\SCN\end{matrix}\!\!>\!CoEn_2\right]X,$$

$$\left[\begin{matrix}H_2O\\O_2N\end{matrix}\!\!>\!CoEn_2\right]X_2,\quad \left[En_2Co\begin{matrix}.NH_2.\\.OH.\end{matrix}\!\!>\!CoEn_2\right]X_4,$$

$$\left[En_2Co\begin{matrix}.NO_2.\\.NH_2.\end{matrix}\!\!>\!CoEn_2\right]X_4$$

By classifying all these series of compounds according to the radical types which characterize them, we obtain the following summary:

a. Compounds with the complex radicals $\left[\begin{matrix}A\\B\end{matrix}\!\!>\!MeEn_2\right]$ (asymmetric metallic atom):

(1) $\left[\begin{matrix}Cl\\H_3N\end{matrix}\!\!>\!CoEn_2\right]X_2$, (2) $\left[\begin{matrix}Br\\H_3N\end{matrix}\!\!>\!CoEn_2\right]X_2$, (3) $\left[\begin{matrix}Cl\\O_2N\end{matrix}\!\!>\!CoEn_2\right]X$,

(4) $\left[\begin{matrix}Cl\\SCN\end{matrix}\!\!>\!CoEn_2\right]X$, (5) $\left[\begin{matrix}O_2N\\SCN\end{matrix}\!\!>\!CoEn_2\right]X$, (6) $\left[\begin{matrix}H_2O\\H_3N\end{matrix}\!\!>\!CoEn_2\right]X_2$,

(7) $\left[\begin{matrix}H_2O\\O_2N\end{matrix}\!\!>\!CoEn_2\right]X_2$, (8) $\left[\begin{matrix}H_2O\\SCN\end{matrix}\!\!>\!CoEn_2\right]X_2$,

(9) $\left[En_2Co\begin{matrix}.O_2.\\.NH_2.\end{matrix}\!\!>\!CoEn_2\right]X_4$, (10) $\left[En_2Co\begin{matrix}.OH.\\.NH_2.\end{matrix}\!\!>\!CoEn_2\right]X_4$,

(11) $\left[En_2Co\begin{matrix}.NO_2.\\.NH_2.\end{matrix}\!\!>\!CoEn_2\right]X_4$

b. Compounds with complex radicals $[A_2MeEn_2]$ (molecular asymmetry I):

(1) $\left[\begin{matrix}O_2N\\O_2N\end{matrix}\!\!>\!CoEn_2\right]X$, (2) $\left[\begin{matrix}Cl\\Cl\end{matrix}\!\!>\!CoEn_2\right]X$, (3) $\left[OC\begin{matrix}O\\O\end{matrix}\!\!>\!CoEn_2\right]X$,

(4) $\left[\begin{matrix}H_3N\\H_3N\end{matrix}\!\!>\!CoEn_2\right]X_3$, (5) $\left[\begin{matrix}Cl\\Cl\end{matrix}\!\!>\!CrEn_2\right]X$

c. Compounds with complex radicals $[MeEn_3]$ (molecular asymmetry II):

(1) $[CoEn_3]X_3$, (2) $[CrEn_3]X_3$, (3) $[RhEn_3]X_3$, (4) $[Dip_3Fe]X_2$

We thus know, in all, the two active forms of 20 series of metallic compounds, and these compounds are derived from 4 different elements: cobalt, chromium, iron and rhodium.

Characteristics of the Active Metallic Compounds

After this general summary of the active compounds thus far obtained, we pass to the characterization of these compounds.

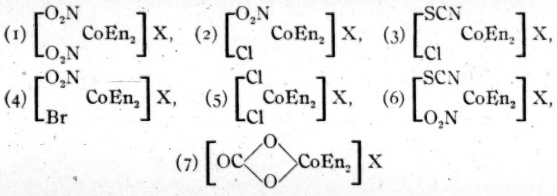
a. Cobalt Compounds

The active compounds derived from cobalt which we have prepared may be classified in the following manner:

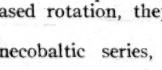
1. Diacidotetraminecobaltic series.
2. Acidopentaminecobaltic series.
3. Hexaminecobaltic series.
4. Series of active compounds with two asymmetric cobalt atoms.

5. Series of active compounds with asymmetric carbon and cobalt.

Of the diacidodiethylenediaminecobaltic salts, we may mention the following:



The stability of these compounds, dissolved in water, is very different. Thus, the dinitrodiethylenediaminecobaltic salts can stand for months in aqueous solution without their rotatory power undergoing any change, while, on the other hand, the nitroisosulphocyanodiethylenediaminecobaltic salts are already less stable, for after four months we observed a decrease of rotatory power amounting to about one-fourth of the initial rotatory power.

The salts of the chloronitro series behave in a still different manner. The optical activity increases rapidly to a maximum value, which is about twice the first value; they show, therefore, the phenomenon of mutarotation. It has been possible to determine the cause of this phenomenon; we have isolated the salts with increased rotation, they belong to the nitroaquodiethylenediaminecobaltic series,  . The phenomenon of mutarotation is therefore the result of a hydration. But the nitroaquodiethylenediaminecobaltic series undergoes, in aqueous solution, an ever-increasing racemization, so that the rotatory power, after having attained a maximum, again diminishes, disappearing completely at the end of a certain time (2 days).

The dichloro series, $[Cl_2CoEn_2]X$, behaves in an entirely different manner. The rotatory power, which is at first very large, diminishes rapidly and disappears completely after a few hours. We have here, therefore, a case of complete racemization taking place very rapidly. Likewise, the active salts of the carbonatodiethylenediaminecobaltic series behave in a very interesting manner. They are stable in cold aqueous solution, but if their solutions are heated the activity

diminishes and it disappears completely if the temperature is raised to 90°. We have determined that the product formed is of the racemic carbonate series, and it is formed without its being possible, as in the other series, to observe the formation of intermediate aquocobaltic salts. This phenomenon of racemization completely resembles, therefore, the phenomena of autoracemization observed in organic chemistry. Let us pass, now to an analysis of the chemical reactions of the active diacidocobaltic compounds. In the chloronitro compounds, we can substitute the chlorine by other acid radicals without the production of any marked racemization. Thus, by the action of sodium nitrite are obtained the active dinitro salts and by the action of potassium sulphocyanate the active nitroisosulphocyanates:

$$\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{O_2N}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X} + \mathrm{NaNO_2} = \left[\begin{matrix}\mathrm{O_2N}\\ \mathrm{O_2N}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X} + \mathrm{NaCl}$$

$$\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{O_2N}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X} + \mathrm{KCNS} = \left[\begin{matrix}\mathrm{SCN}\\ \mathrm{O_2N}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X} + \mathrm{KCl}$$

For the chloroisosulphocyanates, the reactions do not take place so sharply. Thus with sodium nitrite is obtained, besides the active nitroisosulphocyanate series, the racemic series also. The same thing occurs with the active dichloro salts which, with potassium carbonate, give much of the racemic carbonate together with a small quantity of the active salt. A complete racemization takes place when hydrochloric acid in alcoholic solution is made to react on a salt of the active carbonate series; completely inactive 1,2-dichloro salt is formed. In the same way the action of dilute mineral acids on the active carbonate salts produces only inactive diaquodiethylenediaminecobaltic salts. All these facts show that, in certain reactions, intramolecular replacements in the asymmetric radicals take place very easily.

The active acidopentamine compounds which we have thus far prepared correspond to the formulas

$$\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{H_3N}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X_2} \text{ and } \left[\begin{matrix}\mathrm{Br}\\ \mathrm{H_3N}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X_2}$$

These compounds are stable in cold or slightly warm aqueous solution; however, when they remain a long time in solution, they are partially transformed into aquoamminediethylenediaminecobaltic salts, but without undergoing racemization. By the action of silver nitrate it is possible to transform the

bromo series into the aquoamminecobaltic series which we were able to isolate in the pure state. (Its salts show in 0.5 per cent. solution a mean rotatory power $[\alpha]_D = 64°$ and $[M]_D = 392°$.)

If, on the other hand, the aquoamminecobaltic series is prepared by the action of an alkali on the bromo salts in concentrated solution, total racemization occurs. There seems to be here an important starting point for the experimental study of the problem of Walden's optical inversion.

The way in which the bromo series behaves when it reacts with liquid ammonia is very interesting. There are formed the two stereochemical isomers of the diamminediethylenediaminecobaltic series, and while the *cis* form shows a rotatory power, the *trans* form is, as demanded by the theory, entirely optically inactive.

The group of active cobalt compounds with trivalent complex radicals obtained thus far consists of the following series:

$$[CoEn_3]X_3,\ \left[Co\begin{matrix}(NH_3)_2\\ En_2\end{matrix}\right]X_3,\ \left[\begin{matrix}HOH_2N\\ H_3N\end{matrix}CoEn_2\right]X_3,\ \left[Co\begin{matrix}Tn\\ En_2\end{matrix}\right]X_3,$$

$$\left[Co\begin{matrix}Pn\\ En_2\end{matrix}\right]X_3,\ \left[\begin{matrix}H_2O\\ H_3N\end{matrix}CoEn_2\right]X_3$$

The triethylenediaminecobaltic series shows the strongest rotation (bromide, $[\alpha]_D = 117°$, $[M]_D = 600°$), and the amminehydroxylaminediethylenediaminecobaltic series has a rotatory power almost as large (bromide in 0.25 per cent. solution, $[\alpha]_D = 112°$, $[M]_D = 545°$). The diamminediethylenediaminecobaltic series shows the smallest rotatory power (bromide, $[\alpha]_D = 38°$, $[M]_D = 172°$).

Let us consider now the cobalt compounds with complex radicals containing two asymmetric cobalt atoms.

By causing ethylenediamine to react on the octammine-μ-aminodicobaltic salts are obtained tetraethylenediamine-μ-aminoperoxodicobaltic salts. The general formula for these salts is the following:

$$\left[\begin{matrix}^{III}.NH_2.^{IV}\\ En_2Co\quad\quad CoEn_2\\ .O_2\ .\end{matrix}\right]X_4$$

containing two asymmetric cobalt atoms. It has been possible to resolve this series by means of the bromocamphorsulphonates into two active forms with opposite rotatory powers.

These active forms have a rotatory power of exceptional magnitude; the bromides, for example, show a specific rotatory

power of 824°, whence is obtained a molecular rotatory power of 6725°.

Still more interesting results have been obtained with the tetraethylenediamine-μ-aminonitrodicobaltic salts, which were prepared by the action of nitrous acid on the tetraethylenediamine-μ-aminoperoxodicobaltic series. They have a strong red-orange color. We have obtained three different *d*-bromocamphorsulphonates:

1. A difficultly soluble *d*-bromocamphorsulphonate derived from the *d*-μ-aminonitro series.

2. A much more easily soluble *d*-bromocamphorsulphonate derived from the *d*-aminonitro series. The salts prepared from these two bromocamphorsulphonates have equal but opposite rotatory powers.

3. A *d*-bromocamphorsulphonate of intermediate solubility, which gives inactive μ-aminonitro salts not resolvable into active forms.

By combining the active *d*- and *l*-salts, there are obtained racemic salts which are different from the inactive salts derived from the bromocamphorsulphonate of intermediate solubility.

We therefore have here a case analogous to that of the tartaric acids. We have, on the one hand, two active forms with opposite rotatory powers which, in equimolecular mixture, give a racemic form corresponding to "racemic acid." On the other hand, we have a series which is inactive by intramolecular compensation and corresponds to mesotartaric acid or "nonresolvable tartaric acid."

We may conclude from these facts that the constitutional formula of the tetraethylenediamine-μ-aminonitro series is symmetrical, i. e., that the nitro group is combined in the same way to the two cobalt atoms.

Let us note, likewise, that it is possible to transform the active salts into nonresolvable salts, a fact analogous to that observed for the tartaric acids by Jungfleisch, who, by heating tartaric acid at 200°, obtained mesotartaric acid. In the case we are considering, the transformation takes place under analogous conditions, for by vigorously boiling a solution of one of the active salts, a part of the active salt is transformed into a nonresolvable salt.

Let us conclude our summary of the results obtained with the active cobalt salts by adding that we have likewise prepared compounds containing at the same time a complex asymmetric radical and an asymmetric carbon, by the action of active propylenediamine on the dichlorodiethylenediamine-

cobaltic salts. As the propylenediamine enters the complex radical in the *cis* position, the two molecules of ethylenediamine which belong to the complex are perforce in the positions which condition the asymmetric arrangement of the complex radical. But as this arrangement leads to two stereochemical configurations, we should expect the formation of two isomeric active series, *D-l* and *L-d*, the salts of which should be distinguished by their optical activities.

These theoretical previsions have been confirmed experimentally. We obtained two series, which are distinguished especially by the different solubilities of their salts and their optical activity.

b. Chromium Compounds

Thus far we have been able to prepare the optical isomers of two series of chromium compounds. They are the dichlorodiethylenediaminechromic salts, which show the molecular asymmetry I, and the triethylenediaminechromic salts, which exhibit the molecular asymmetry II. The dichlorodiethylenediaminechromic salts are very slightly stable in aqueous solution, like their analogues in the cobaltic series. Their molecular rotatory power, which is about 500°–600°, decreases very rapidly, and after a few hours the solutions have become entirely inactive. It is probable that this phenomenon of racemization is the result of the intermediate formation of hydrated salts; however, we still lack a thorough experimental study of this subject.

The triethylenediaminechromic salts are, on the contrary, much more stable. Their molecular activity in cold aqueous solution is about 340° and hardly undergoes any change on long standing of the salts in solution. It is only when the solutions are evaporated that the optical activity diminishes.

c. Iron Compounds

All the active compounds of cobalt and chromium thus far obtained contain ethylenediamine as a constituent group of the complex molecule. It was therefore important to effect the resolution of compounds containing in the place of ethylenediamine other coördinately bivalent groups and to prove thus that the ethylenediamine is not absolutely necessary for the formation of active metallic compounds. Moreover, in order to be able to study the influence of the central atom on the rotatory power of complex inorganic compounds, it was desirable to prepare optically active compounds derived from other metallic elements.

These considerations led us to attempt the resolution of

the tri-α-dipyridylferrous compounds, $[FeDpy_3]X_3$. The discovery of these iron compounds is due to F. Blau, and they present a more general interest because they possess an intense red color and contain the iron in a masked form, recalling the properties of hemoglobin. After numerous unsuccessful attempts, we have been able to prepare the tartrate of the *l*-rotatory series of irontri-α-dipyridyl by saturating the aqueous solution of the racemic bromide with ammonium *d*-tartrate. It was possible to transform the tartrate thus obtained into different salts, such as the iodide, the bromide, etc., and these salts were found to possess a very large rotatory power. The specific rotatory power varies around 500°, which, for the bromide, corresponds to a molecular rotatory power of 4000°.

In the solid state, these iron salts remain active indefinitely, but in aqueous solution they racemize very rapidly. After one-half hour, the rotatory power has already decreased by one-half, and after a few hours the solutions of these salts have become entirely inactive. This phenomenon of racemization is certainly caused by a partial decomposition of the active salts, with separation of a small quantity of α-dipyridyl, which, in aqueous solution, forms a dynamic equilibrium with the nondecomposed tri-α-dipyridylferrous salt. Our further studies must be applied to the investigation of active iron compounds showing greater stability.

The results obtained thus far with iron compounds show that the iron atom can likewise function as the center of asymmetric molecules showing optical activity. Moreover, they show that the activity of the optical isomers thus far described is not related with the specific nature of ethylenediamine but that the phenomenon also manifests itself when the ethylenediamine is replaced by other groups. Finally, let us emphasize the fact that in the iron compounds we have to do with derivatives of a bivalent metallic atom, while the active compounds of the other elements are derived from tri- and tetravalent metallic atoms.

d. Rhodium Compounds

Although we do not, up to the present, know any rhodium compounds containing groups with two coördinative valences, we have been able to prepare the triethylenediaminerhodic salts. If sodium chlororhodiate, $[RhCl_6]Na_3$, is introduced into monohydrated ethylenediamine, it dissolves rapidly with evolution of heat and formation of a slightly yellow solution. This solution contains triethylenendiaminerhodic chloride, $[RhEn_3]Cl_3$, which can be isolated in beautiful, colorless crys-

tals. It has been possible to obtain the active triethylenediaminerhodic salts by two different methods.

The first consists in precipitating the concentrated solution of the chloride with sodium camphornitronate. The camphornitronate which separates belongs to the levo series and by adding potassium iodide to the mother liquor the iodide of the dextro series is obtained.

The resolution is still better effected by the method used for the resolution of the triethylenediaminecobaltic salts. Triethylenediaminerhodic chloride is made to react with a molecule of silver tartrate and the solution is concentrated until crystals are formed. The chloride-tartrate of the levo series separates in the form of colorless crystals, very clear and beautifully developed; the concentrated mother liquor gives a white salt of chalky appearance, which is the chloride-tartrate of the dextro series.

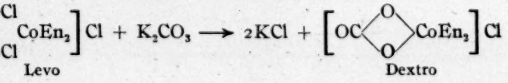
The chloride-tartrates can easily be transformed into other salts. The specific rotatory power of these salts varies between 70° and 80°, which corresponds to a molecular rotatory power of about 300°.

Relations between the Optical Activity, the Configuration and the Constitution of the Complex Inorganic Compounds

The greater number of the active metallic compounds which we have studied contain a complex radical $[MeEn_2]$, whose formula in space is not superposable on its image and can thus present itself under two stereochemical forms.

We might inquire if all the compounds presenting the same configuration of the radical $[MeEn_2]$ deviate the plane of polarized light in the same direction. We were easily able to establish that this is not the case, but that the direction of the rotatory power depends on the nature of the radicals which occupy the two other coördination positions of the central atom and on the nature of that central atom.

This is derived from the fact that we have been able to prepare compounds of opposite rotatory powers by chemical reactions which are certainly not accompanied by a change in configuration. Let us give some examples: Starting from the *l*-dichlorodiethylenediaminecobaltic series, we have obtained, by making it react with potassium carbonate, the *d*-carbonatodiethylenediaminecobaltic series:



Levo Dextro

Likewise, the *l*-chloroisosulphocyanodiethylenediaminecobaltic salts are transformed, by the action of sodium nitrite, into *d*-nitroisosulphocyanodiethylenediaminecobaltic salts:

$$\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{SCN}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X} + \mathrm{NaNO_2} \longrightarrow \mathrm{NaCl} + \left[\begin{matrix}\mathrm{O_2N}\\ \mathrm{SCN}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X}$$

Levo Dextro

Moreover, by reduction of the salts of the *l*-tetraethylenediamine-μ-aminoperoxodicobaltic series are obtained the salts of the *d*-tetraethylenediamine-μ-amino-oldicobaltic series:

$$\left[\mathrm{En_2Co}\begin{matrix}\mathrm{O_2}\\ \mathrm{NH_2}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X_4} \longrightarrow \left[\mathrm{En_2Co}\begin{matrix}\mathrm{OH}\\ \mathrm{NH_2}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X_4}$$

Levo Dextro

Finally, by the action of nitrous acid on the tetraethylenediamine-μ-aminoperoxodicobaltic salts is obtained, starting from the *l*-series, the *d*-series of tetraethylenediamine-μ-aminonitrodicobaltic salts:

$$\left[\mathrm{En_2Co}\begin{matrix}\mathrm{O_2}\\ \mathrm{NH_2}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X_4} \longrightarrow \left[\mathrm{En_2Co}\begin{matrix}\mathrm{NO_2}\\ \mathrm{NH_2}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X_4}$$

Levo Dextro

On the other hand, we have been able to establish the following interesting law: the active isomeric series which give, with the same active acids, the less soluble salts show the same stereochemical configuration of the radical [$\mathrm{MeEn_2}$]. This law is demonstrated by the following facts:

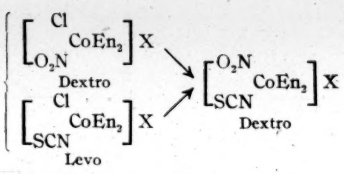
The *d*-chloronitro series and the *l*-chloroisosulphocyano series give with *d*-bromocamphorsulphonic acid salts which are much less soluble than those formed with the *l*-acid. It is proved that they correspond to the same stereochemical configuration by the fact that, by the action of potassium sulphocyanide on a salt of the *d*-chloronitro series and of sodium nitrite on a salt of the *l*-isosulphocyano series, the same *d*-rotatory nitroisosulphocyano series is obtained:

$$\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{O_2N}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X} + \mathrm{KSCN} = \mathrm{KCl} + \left[\begin{matrix}\mathrm{SCN}\\ \mathrm{O_2N}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X}$$

$$\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{SCN}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X} + \mathrm{KNO_2} = \mathrm{KCl} + \left[\begin{matrix}\mathrm{O_2N}\\ \mathrm{SCN}\end{matrix}\mathrm{CoEn_2}\right]\mathrm{X}$$

These transformations may be represented by the following scheme:

Give difficultly soluble *d*-bromocamphorsulphonates



Another fact of the same nature is the following: the *l*-tetraethylenediamine-μ-aminoperoxodicobaltic series furnishes a difficultly soluble *d*-bromocamphorsulphonate, while the *d*-tetraethylenediamine-μ-aminonitrodicobaltic series gives a difficultly soluble *d*-bromocamphorsulphonate.

Now, the *l*-tetraethylenediamine-μ-aminoperoxodicobaltic series is transformed by the action of nitrous acid into the *d*-tetraethylenediamine-μ-aminonitrodicobaltic series, proving that the configuration of the $[CoEn_2]$ groups of these series is identical.

We may summarize the phenomena observed in the following manner: The compounds of the series with identical asymmetry show parallel processes of solubility in their salts with active acids, but the direction of the rotatory power of the salts in question is not necessarily the same.

It is on the basis of these new ideas that we can study in more detail the relations between the rotatory power and the composition of the asymmetric molecules.

Classifying the series with identical configuration in the order of the magnitude and direction of their molecular rotatory powers, we obtain the following summary:

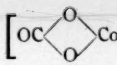
$$\left[En_2Co\begin{matrix}OH\\NH_2\end{matrix}CoEn_2\right]X_4,\ [Cl_2CoEn_2]X,\ [Cl_2CrEn_2]X,\ [RhEn_3]X,$$

$$\underset{-6723^\circ}{\left[\begin{matrix}Cl\\SCN\end{matrix}CoEn_2\right]X_2},\quad \underset{-550^\circ}{\left[\begin{matrix}Cl\\O_2N\end{matrix}CoEn_2\right]X_2},\quad \underset{-400^\circ}{\left[\begin{matrix}H_2N\\H_2O\end{matrix}CoEn_2\right]X_2},\quad \underset{-350^\circ}{}$$

$$\underset{-200^\circ}{\left[\begin{matrix}O_2N\\O_2N\end{matrix}CoEn_2\right]X},\quad \underset{+74^\circ}{\left[\begin{matrix}O_2N\\H_2O\end{matrix}CoEn_2\right]X_2},\quad \underset{+124^\circ}{\left[\begin{matrix}H_2N\\H_2N\end{matrix}CoEn_2\right]X_2},$$

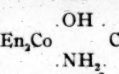
$$\underset{+145^\circ}{\left[\begin{matrix}H_2N\\Cl\end{matrix}CoEn_2\right]X_2},\quad \underset{+165^\circ}{\left[\begin{matrix}H_2N\\Br\end{matrix}CoEn_2\right]X_2},\quad \underset{+172^\circ}{\left[\begin{matrix}O_2N\\SCN\end{matrix}CoEn_2\right]X},$$

$$+172^\circ. \qquad +180^\circ \qquad +200^\circ$$

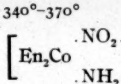


$+280°$

$[CrEn_3]X_3$, $+340°$–$370°$ $[CoEn_3]X_3$, $+600°$



$+990°$



$+1300°$–$1400°$

As a result, the rotatory power is seen to vary between very wide limits and all the groups forming part of the asymmetric complex radical have an influence on the value of the rotatory power. It is seen, likewise, that the nature of the central atom has a capital influence on the magnitude and the direction of the rotatory power, for the rotatory powers of the triethylenediaminecobaltic, -chromic and -rhodic salts, as well as those of the dichlorodiethylenediaminecobaltic and -chromic salts, are entirely different. The compounds of chromium have a smaller rotatory power than the cobalt compounds, but this difference is not equal in the different series; it is about 150° for the dichloro salts, while it is about 250° for the salts containing the triethylenediamine complex radical. The magnitude of the rotatory powder depends, therefore, on a special factor, the value of which is determined by the particular relations which exist between the central atom and the groups which it unites in the complex radicals.

Let us add that the triethylenediaminerhodic salts deviate the plane of polarized light almost as much to the left as the triethylenediaminechromic salts of the same configuration deviate it to the right.

The values for the rotatory powers which served for our theoretical deductions were determined under experimental conditions as nearly comparable as possible; nevertheless, these values probably do not yet give an exact measure of the relative magnitudes of these rotatory powers, and this for the following reasons: The magnitude of the rotatory power often depends to a very high degree on the concentration of the solutions of the salts, and, as near as we can judge thus far, the activity is greater the more dilute the solution. This is probably due to the compounds in the undissociated state having a smaller rotatory power than their asymmetric cations, and it will be necessary, therefore, in order to obtain comparable values, to determine the rotatory power of the undissociated compounds and of their cations. Moreover, it is to be noted that almost all the compounds studied thus far are colored and show very large rotatory dispersions, so that it will be neces-

sary to make exact studies on the relations which exist between the magnitude of the rotatory power and the wave length of the light.

I hope that the researches which we have begun in this direction will lead to precise ideas on the influence of the different atomic groups of the complex radicals on the optical activity.

To end our review, let us consider briefly the consequences of the results thus far obtained for the theory of valence and for stereochemistry.

Our experiments show in the first place that it is of secondary importance for the stability of the molecules of the complex compounds whether the atoms are united by principal valences or by secondary valences. For the study of the structure of inorganic compounds, secondary valences assume an equal importance with principal valences. This naturally leads us to admit that there is no essential difference between the affinities brought into play by the principal valences and the secondary valences. We probably have to do with affinity forces which are distinguished only in magnitude and not in quality and the difference between which does not manifest itself in any notable manner except when the atomic unions which they produce are so different that the ones lead to compounds of great stability and the others to compounds which are slightly stable.

The question of knowing what secondary causes (migrations of electrons, etc.) may lead to a more pronounced differentiation between the atomic unions produced by principal and secondary valences is independent of the question of the nature of the affinity forces which determine the structure of complex inorganic molecules.

As to what concerns stereochemistry, our studies have led us to the probable conclusion that all elementary atoms, in so far as they can function as the central atom of stable complex radicals, are capable of forming compounds showing optical isomerism. Moreover, it has been shown that the optical isomerism is not necessarily due to the different nature of the groups combined with the central atom, but that every asymmetric configuration leads to optical isomerism, even if the constituent parts of the molecular grouping are equal.

We come back then, to the principle which Pasteur first formulated and which admits that every molecule having no plane of asymmetry, i. e., showing structural asymmetry, must always exist in the form of two oppositely active optical modifications. The isomerism phenomena related with the molec-

ular asymmetry of metallic compounds, with asymmetric cobalt, with asymmetric carbon, with asymmetric nitrogen, with the molecular asymmetry of the inositols, etc., are therefore only special cases resulting from this general principle, a principle from which the possibility of numerous other cases of optical isomerism can still be predicted.

The end of future investigations, then, will be to determine what other new cases of optical isomerism, foreseen through our conceptions on the arrangement in space of inorganic molecules, can be realized experimentally.

OBITUARY

L. P. CAILLETET[1]

L. P. Cailletet, known to all chemists and physicists by his work on the liquefaction of gases, died on January 5th, after a short illness. He was born at Châtillon-sur-Seine, September 21, 1832, and thus lived to be over 80 years of age. From his earliest youth he was familiar with the processes involved in blast furnaces and the working of iron. He studied in Paris at the Ecole Superiéure des Mines and his first scientific work was in connection with the cementation and puddling processes. He showed that iron is permeable to gases at high and low temperatures. He next undertook the study of the properties of gases under high pressures. In the course of this work he developed the method for the liquefaction of gases based on the principle of the sudden expansion of the compressed gas. His results with carbon dioxide, carbon monoxide and oxygen were embodied in a sealed communication which was opened December 27, 1877, on receipt of the news that Pictet, of Geneva, had likewise effected the liquefaction of oxygen. About this time, Mathias became associated with Cailletet as his assistant and within the next few years these two men carried out their famous work on the liquefaction of the so-called permanent gases.

In 1893 Cailletet began a series of studies on the resistance offered by the air to moving bodies. By means of balloons carrying ingeniously devised forms of apparatus, he was able to obtain samples of air from different heights and to get accurate thermometric and barometric data and even photographs. He founded what eventually became an International Commission of Scientific Aeronautics for the purpose of making systematic meteorological observations with test balloons. His activities in these lines brought him into prominence in

[1] This note is based on a sketch by Raoult Pictet in the Chem. Ztg., 37, 177.

the Aero Club of France, and he exerted a most beneficial influence in its affairs.

REVIEWS

CHURCH'S LABORATORY GUIDE, a Manual of Practical Chemistry for Colleges and Schools, Especially Arranged for Agricultural Students. Revised and Largely Rewritten by EDWARD KINCH, F.I.C., etc., Professor of Chemistry in the Royal Agricultural College, Cirencester. Ninth Edition. New York: D. Van Nostrand Co. 1912. xvi + 368 pp. Price, $2.50.

This book is divided into three parts: Part I, 68 pages, contains introductory laboratory experiments, such as specific gravity, preparation of oxygen and hydrogen, ashes of plants, etc.; Part II, 70 pages, deals with qualitative analysis; Part III, 216 pages, takes up quantitative analysis, and gives methods for fertilizers, feeds, soils, etc. The methods of analysis for fertilizers and feeds are those prescribed by the English Board of Agriculture and Fisheries. They are quite different in some respects from the methods of the Official Agricultural Chemists of North America. The book is intended to include a complete course of laboratory practice for agricultural students. The fact that it has gone into nine editions shows that it has been useful. G. S. F.

ELEMENTARY CHEMICAL THEORY AND CALCULATIONS. By JOSEPH KNOX, D.Sc., Lecturer on Inorganic Chemistry, University of Aberdeen. London: Guerney and Jackson. 1912. pp. vii + 102. Price, 2s.

The author has made a collection of well selected chemical problems and has given a clear explanation of the laws and principles upon which their solution is based. J. E. G.

GRUNDZÜGE DER PHARMAZEUTISCHEN CHEMIE. Von HEINRICH BECKURTS, Geheimer Medizinalrat, o. Professor der pharmazeutischen Chemie und Vorstand des Pharmazeutischen Institutes der Herzogl. Technischen Hochschule zu Braunschweig. Mit 15 Abbildungen im Text und 1 Spektraltafel. I. Band. Anorganische Teil. Leipzig: Verlag von S. Hirzel. 1912. S. xix + 386. Preis, geh., M. 10; geb., M. 11.

As is indicated by the title, this book is intended especially for the student of pharmacy and places special emphasis on the qualitative and quantitative tests as to purity and adulterations, as well as the determination of factors such as melting point, boiling point and specific gravity, according to the requirements of the Pharmacopoeia. J. E. G.

INTRODUCTION TO THE RARER ELEMENTS. By PHILIP E. BROWNING, PH.D., Assistant Professor of Chemistry, Kent Chemical Laboratory, Yale University. Third edition, thoroughly revised. New York: John Wiley & Sons. London: Chapman & Hall, Ltd. 1912. pp. xii + 232. Price, $1.50.

Dr. Browning's book needs little description, so far as the

general characteristics are concerned, to those who have made even a cursory study of the rarer elements. Since the first edition was printed in 1903, it has been before every student of chemistry and has invariably made friends.

The third edition is welcome and contains valuable additions. The new tables and charts of both spark and absorption spectra will prove invaluable to the student wishing to make spectroscopic comparisons. The enlargement of the methods of qualitative separation and of the technical applications of the rarer metals, the inclusion of James' latest chart for the fractionation of the rare earths, and the numerous minor changes and enlargements caused by the advance in chemical knowledge since the last edition appeared, all give additional value to the book.

There is little for the reviewer to criticize for the book is already much more than its title would imply and the work is well done. It may not be amiss, however, to hope that in the next edition Professor Browning may carry much farther the work which he is so capable of doing. Scandium, for example, might well be separated from the rare earths, to which it scarcely belongs, and given a chapter by itself, as is already done with the much rarer element germanium; and the recent work of Sir William Crookes would alone furnish much of the material needed for such a presentation. Considering the growing commercial importance of tungsten and vanadium, the subject matter regarding these two elements could be materially expanded; and this is true of most of the other elements considered. In short, we need in the English language a book whose correct title should be "The Rarer Elements" with "Introduction to" left off.

Let us hope that the next edition will cover completely this subject which Professor Browning can handle so well.

CHARLES L. PARSONS

A SECOND YEAR COURSE OF ORGANIC CHEMISTRY FOR TECHNICAL INSTITUTES. The Carbocyclic Compounds. By F. B. THOLE, B.Sc. (Lond.), Lecturer in Organic Chemistry at the East Ham Technical College. London: Methuen & Co., Ltd. 1912. pp. vii + 186. Price, 2 s. 6 d.

This compact and business-like little volume is one of a series of text-books on Organic Chemistry and is chiefly devoted to the compounds of the aromatic series, though it also contains chapters devoted to the polymethylenes, the Grignard reaction, a list of glucosides, and a brief treatise upon Organic Qualitative Analysis.

The work has obviously been prepared chiefly for use in the author's own classes so that it would not be appropriate

to comment critically upon the selection and arrangement of the topics presented. The reviewer, however, believes that its general usefulness will be somewhat restricted on this account.

The book gives concise and definite information concerning the important organic compounds and those theories which it attempts to treat, but the author has allowed himself to yield to the student's craving for unqualified generalizations to an extent which sometimes goes beyond the limits of accuracy. It is only fair to add that the facts which should have qualified some of these statements are usually to be found in other portions of the book.

In spite of this defect, the work seems to be a useful and essentially accurate treatise, and the author is especially to be commended for the amount of space which he gives to the subject of Organic Qualitative Analysis. No method of approaching the subject is so well adapted as this to arouse the student's interest, and none teaches so much chemistry in so short a time.

F. J. MOORE

UNTERSUCHUNGEN ÜBER DIE BILDUNGSVERHÄLTNISSE DER OZEANISCHEN SALZABLAGERUNGEN insbesondere des Stassfurter Salzlagers. Von J. H. VAN'T HOFF. Herausgegeben von PROFESSOR DR. H. PRECHT, Neustassfurt, und PROFESSOR DR. ERNST COHEN, Utrecht. Mit einer Gedächtnisrede auf van't Hoff von PROFESSOR DR. EMIL FISCHER, Exz. Mit 8 Tafeln und 39 Textabbildungen. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1912. pp. xx + 374. Price, M. 16.

Van't Hoff published, during the years 1897–1908, a series of fifty-two papers dealing with investigations of conditions of formation of oceanic salt deposits. In the conduct of these researches he was assisted by twenty-nine collaborators (of whom it may be noted that English is the native language of at least twelve), and received financial aid from the Königliche Preussische Akademie der Wissenschaften, in whose *Sitzungsberichte* the original papers appeared. These transactions are not generally accessible, and the individual papers are all out of print. A short account of the work was given in two pamphlets published by van't Hoff, one in 1905 and one in 1909, under the title "Zur Bildung der ozeanischen Salzablagerungen," but this extract is not full enough for any one desirous of studying the methods and results in detail. These considerations have led to the publication of the present volume, which contains all of the original papers in full, together with a prefatory note by the editors and an introductory memoir of van't Hoff written by Emil Fischer.

It is unnecessary to give here the titles of the separate papers, since their general tenor is well known; it suffices to

say that they deal with the chlorides and sulphates, and to a lesser extent the borates, of potassium, sodium, magnesium and calcium, their relations to water and to one another. The experimental work was carried out mainly at 25°, but also to some extent at higher temperatures up to 83°; it consists almost entirely of determinations of solubility, of vapor pressure by means of the tensimeter, and of transition points directly by means of the dilatometer. This series of investigations is an object lesson in showing us what may be accomplished with simple experimental means by the thoroughgoing application of certain chemical principles and is an admirable example of the way to attack similar complex problems, to correlate and interpret the observations, and thus to reach conclusions of great significance—all of which would not have been attained except with the aid of these theoretical principles.

In the introduction to the first paper van't Hoff, in 1897, wrote: "When a thorough series of physico-chemical investigations has led to some knowledge of the equilibrium relations which hold when salts enter into, or separate from, aqueous solutions, and determine the formation of hydrates and double salts and the nature of products obtained by double decomposition, then something can be contributed from the physico-chemical side towards the solution of the geologic problem of the formation of the complex natural salt beds." This modest aspiration has been more than fulfilled. Indeed the success attained by van't Hoff in clearing up this problem is such that we are only now beginning to realize its consequences—technical, economic and scientific; of which not the least is that it has stimulated the investigation of complex systems and encouraged people to attack problems which, until recently, were considered insoluble. In conclusion, it may be noted that the experimental work recorded in this volume is now being repeated and amplified under the direction of the "Verband zur wissenschaftlichen Erforschung der deutschen Kalisalzlagerstätten," the formation and plans of which are discussed in the fifty-second and last paper in the volume.

JOHN JOHNSTON

THE FREEZING-POINT, BOILING-POINT AND CONDUCTIVITY METHODS. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. Second edition, completely revised. Easton, Pa.: Chemical Publishing Co. 1912. pp. vii + 75. Price, $1.00.

The appearance of a second, completely revised edition of this booklet will be welcomed in all physico-chemical laboratories. When it first appeared it was the pioneer laboratory

manual of physical chemistry in the English language and as such was cordially received. Notwithstanding the fact that numerous laboratory manuals are now on the market, this little volume still fills an important place. In the new edition several minor corrections have been made, more comprehensive tables of cryoscopic and ebullioscopic constants have been included and an account is given of the author's extension of the boiling-point method to the measurement of ionization in nonaqueous solvents. The chapter devoted to the measurement of electrical conductivity has been subjected to a thorough revision, the method used in the author's laboratory being described in detail. The book appears in a durable and attractive binding. FREDERICK H. GETMAN

TRATTATO DI CHIMICO-FISICA. HARRY C. JONES, Professore di Chimico-fisica nella Università di Baltimora. Traduzione italiana con Note del DOTT. MICHELE GIUA, Assistente nel Laboratorio Chimico della Società d'Incorraggiamento in Milano, con Prefazione del PROF. ETTORE MOLINARI e 81 Incisioni nel Testo. Milano: Ulrico Hoepli. 1913. pp. XX + 611.

The appearance of this Italian translation, shortly after the publication of the Russian edition, is evidence of the popularity of Prof. Jones' well-known book not only at home but abroad as well. In his translation, Dr. Giua has closely followed the fourth English edition, merely adding a few notes here and there on some of the latest developments of the science. The translation seems to have been well done and the mechanical make-up of the book is up to the high standard of the Hoepli publications. C. A. R.

DAS ERDÖL UND SEINE VERWANDTEN. Geschichte, physikalische und chemische Beschaffenheit, Vorkommen, Ursprung, Auffindung und Gewinnung des Erdöls. Von DR. h. c. HANS VON HÖFER, k. k. Hofrat, em. o. ö. Professor an der k. k. Montanistischen Hochschule in Leoben. Dritte, vermehrte Auflage. Mit 33 Abbildungen im Text und einer Tafel. Neues Handbuch der Chemischen Technologie (Bolley's chemische Technologie, dritte Folge). Herausgegeben von DR. C. ENGLER, wirkl. geh. Rat und Professor an der Technischen Hochschule Friedericiana in Karlsruhe. IV. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1912. S. xvi + 351. Preis, geh., M. 12; geb., M. 13.50.

The book, as its title states, deals with the properties, occurrence, origin, and methods of finding petroleum and the bitumens rather than with their technology or testing. Particular attention is paid to the geological side, especially to the Hoefer theory of the anticlinal occurrence of petroleum. It may be especially commended to the geologist, the oil-well driller and to any one who desires information about the sub-

ject. It is—particularly the historical part—very interestingly written and apparently no investigator has been overlooked.

It may be cordially commended to those interested in the subject.

A. H. GILL

DIE FABRIKATION DES RUSSES UND DER SCHWARZE aus Abfällen und Nebenprodukten, mit besonderer Berüchsichtigung der Entfärbungskohle. Von DR. HIPPOLYT KÖHLER, Direktor der Rütgerswerke-Aktiengesellschaft, Berlin. Dritte, gänzlich umgearbeitete Auflage. Mit 114 Abbildungen im Text. Neues Handbuch der chemischen Technologie (Bolley's chemische Technologie, dritte Folge), herausgegeben von DR. C. ENGLER, wirkl. geh. Rat und Professor an der Technischen Hochschule Friedericiana in Karlsruhe. V. Braunschweig: Druck und Verlag von Friedr. Vieweg & Sohn. 1912. S. viii + 228. Preis: geh., M. 7; geb., M. 8.

This book is chiefly a more or less academic description of many different methods of manufacturing commercial soots, which are sold in commerce under the names of "Lamp Black" and "Carbon Black."

We think it is the first serious effort to devote a book to this branch of technical industry, although there are a great number of separate articles on the subject to be found in many technical journals and many popular periodicals, most of which articles, however, have been not only inaccurate, but essentially misleading, giving, in many cases, a totally false and inadequate idea of the processes that they profess to describe.

The present volume is an immense improvement over the best previous sources of information as to this interesting and important industry, which gives us the pigments with which our books and periodicals are printed, as well as the basis of most of the black paint of commerce, not to mention many less important uses for this material.

It does not, however, attain the ideal at which the author aimed, to wit, an entirely correct picture of the present condition of this important industry and for the reason that he is evidently without personal experience of the Carbon Black industry, which is almost the sole basis of black printers' inks in this country and becoming yearly more important in this and other branches in Europe.

His own experience in the manufacture of Lamp Black from tar products gives special value to his observations with regard to this branch of the industry, but a better perspective would be given to the picture as a whole if he had included the statistics of production of Lamp Black and Carbon Black throughout the civilized world and some information as to the actual price to large buyers.

The book begins with a very interesting essay on the phenomena of combustion. The largest part of the book is taken up by a compilation of most of the known and described methods of manufacturing Lamp Black from tar, tar-products, etc., by burning with an insufficient supply of air and permitting the soot to settle on suitable chambers.

The American Carbon Black industry, which produces 25 million pounds a year, is very briefly mentioned; no description whatever is given of the most important methods of manufacture and no suggestion of the relative importance of the different methods.

It is a particularly difficult and thankless task to give a complete and well proportioned account of the industries herein treated, because the capital involved and the number of people interested is so much smaller than in many industries which perhaps for mankind are really of less importance, and, further, because the industry in this country has evolved very different methods from those which are in vogue in Europe, with totally different raw materials and with essentially different finished products.

Therefore, to make a thorough, practical study of the industry would imply wide journeys through many different lands and to comparatively inaccessible spots, much more so than is the case with many chemical industries involving much greater amounts of capital and much greater interest for the technical world.

A study, for instance, of the acid and soda industry in England or Germany or the United States would give a very fair idea of the same industry at any point in the civilized world. The black industry, on the other hand, has developed so differently on the two sides of the Atlantic that it would be necessary to study it in different countries in order to get an equally good and well proportioned conception of the whole.

The author deserves much credit for taking a scientific and general view of a somewhat prosaic industry that has been left too much to so-called practical men, who, relying too much on what the untrained eye can see, often miss the fundamentals of the problems that are confronting them and, therefore, repeat by rote, generation after generation, the same fatuous errors.

The reviewer thinks the book is well worth a careful study by any one engaged in the industries that it describes. He dares to say that there is no person extensively engaged in any of these industries that cannot find in it suggestions that will be of value if intelligently grasped and utilized.

He hopes that the author will some time study the industry in this country and give to the world as intelligent and well proportioned a picture of it as he has of European conditions and he closes this brief review by repeating that he thinks the author has performed a somewhat thankless task incomparably better than any previous writer on the subject.

A careful study of this book will show the fundamental facts, that these commercial soots are all, in the last analysis, either made by the combustion of oily or fatty matter with an insufficient supply of air and the slow settling of the smudge thereby produced or by the direct deposition of the carbon from the flame by contact with relatively cold metallic surfaces or by the superheating of hydrocarbons out of contact with air, and a keen appreciation of these fundamentals will save practical manufacturers much useless experimenting and lead to further progress in the industries involved.

GODFREY L. CABOT

THE IRON ORES OF MISSOURI. By G. W. CRANE, Missouri Bureau of Geology and Mines. H. A. BUEHLER, Director. Vol. X, Second Series. Jefferson City, Mo.: Hugh Steffens Printing Co. 1912. pp. xvi + 434.

This book is an excellent report on the iron ores of Missouri, prepared under the direction of the Missouri Bureau of Geology and Mines. It contains an account of the history, development, and production of Missouri iron ores. There is, also, a general discussion of the ores of iron and the factors which control their value. In addition to the general chapters on physiography, geology, and occurrence, distribution and chemical composition of the various types of iron ores, there are descriptions of all the known deposits of the state. The book contains many very good photographs and maps of the different iron-ore regions of Missouri. It contains many interesting facts, and it is to be recommended not only to those interested in mining, but also to those wishing to have at hand a general account of iron ores.

LEROY MCMASTER